– 1 –

The State of the Art

Alessandro Gandini and Mohamed Naceur Belgacem

ABSTRACT

This chapter gives a general introduction to the book and describes briefly the context for which the editors established its contents and explains why certain topics were excluded from it. It covers the main raw materials based on vegetable resources, namely (i) wood and its main components: cellulose, lignin, hemicelluloses, tannins, rosins and terpenes, as well as species-specific constituents, like natural rubber and suberin; and (ii) annual plants as sources of starch, vegetable oils, hemicelluloses, mono and disaccharides and algae. Then, the main animal biomass constituents are briefly described, with particular emphasis on: chitin, chitosan, proteins and cellulose whiskers from molluscs. Finally, bacterial polymers such as poly(hydroxyalkanoates) and bacterial cellulose are evoked. For each relevant renewable source, this survey alerts the reader to the corresponding chapter in the book.

Keywords

Animal biomass, Vegetal biomass, Wood, Cellulose, Lignins, Hemicelluloses, Natural rubber, Suberin, Tannins, Rosins, Terpenes, Annual plants, Starch, Vegetable oils, Hemicelluloses, Mono and disaccharides, Polylactic acid, Algae, Chitin, Chitosan, Proteins, Cellulose whiskers, Bacterial polymers, Poly(hydroxyalkanoates), Bacterial cellulose

1.1 THE CONTEXT

The biosynthesis of macromolecules through enzymatic, bacterial and chemical polymerizations of specific molecular structures constitutes a key step in the evolution of living organisms. Natural polymers have therefore been around for a very long time and always constituted one of the essential ingredients of sustainability, first and foremost as food, but also as shelter, clothing and source of energy. These renewable resources have also played an increasingly important role as materials for humanity through their exploitation in a progressively more elaborated fashion. The ever improving technologies associated with papermaking, textile and wood processing, vegetable oils, starch and gelatin utilization, the manufacture of adhesives, etc. represent clear examples of the progressive sophistication with which man has made good use of these natural polymers throughout the millennia. Concurrently, natural monomers have been polymerized empirically for equally long periods for applications such as coatings, paint and ink setting, leather tanning, etc.

The progress of chemistry, associated with the industrial revolution, created a new scope for the preparation of novel polymeric materials based on renewable resources, first through the chemical modification of natural polymers from the mid-nineteenth century, which gave rise to the first commercial thermoplastic materials, like cellulose acetate and nitrate and the first elastomers, through the vulcanization of natural rubber. Later, these processes were complemented by approaches based on the controlled polymerization of a variety of natural monomers and oligomers, including terpenes, polyphenols and rosins. A further development called upon chemical technologies which transformed renewable resources to produce novel monomeric species like furfuryl alcohol.

The beginning of the twentieth century witnessed the birth of a novel class of materials, the synthetic polymers based on monomers derived from fossil resources, but the progress associated with them was relatively slow up to the Second World War and did not affect substantially the production and scope of the naturally based counterparts. Some hybrid materials, arising from the copolymerization between both types of monomers were also developed at this stage as in the case of the first alkyd resins. Interestingly, both monomers used in the first process to synthesize nylon in the late 1930s were prepared from furfural, an industrial commodity obtained from renewable resources, in a joint venture between Quaker Oats and DuPont.

The petrochemical boom of the second half of the last century produced a spectacular diversification in the structures available through industrial organic chemistry. Among these, monomers played a very significant role, as it transpires from the high percentage of such structures represented in the list of the most important chemical commodities in world production. The availability of a growing number of cheap chemicals, suitable for the production of macromolecular materials, gave birth to 'the plastic age', in which we still live today, with of course greatly enhanced quantitative and qualitative features.

This prodigious scientific and technical upsurge went to the detriment of any substantial progress in the realm of polymers from renewable resources. In other words, although these materials never ceased to exist, very modest investments were devoted to their development, compared with the astronomical sums invested in petrochemistry. As a consequence, although cotton, wool and silk textile are still plentiful, the competition of synthetic fibres has not stopped growing. Likewise, the incidence of natural rubber is very modest today, compared with its synthetic counterparts, not only in relative tonnage, but also in the continuously widening degree of sophistication associated with the properties of the latter materials. In virtually all other domains associated with polymeric materials, the present contribution of structures derived from renewable resources is very modest and has not played an appreciable role in terms of bringing about specific functional properties. On the other hand, paper has resisted all attempts to be replaced by synthetic polymers, although these have been playing a growing role as bulk and surface additives, albeit without modifying the essential constitution of this material, which still relies on the random assembly of cellulose fibres.

We are deeply convinced that this state of affairs has nothing to do with any consideration of relative merits associated with the different structures and chemical processes involved in either context. Its origin is instead to be found in a purely economic aspect (*i.e.* in the enormous difference in investment that favoured petrochemistry for the last half century) which was also the period when the chemical industry witnessed its fastest progress ever. The choice to finance R&D activities in polymers derived from fossil resources in a massive way was to the benefit of the corresponding materials as we know them today. This objective situation, however, does not prove anything against the potential interest of alternative counterparts made from renewable resources, simply because no such investments were ever made to that effect.

Should fossil resources be available for us to exploit for centuries to come, the above arguments would sound like a futile exercise in style. Their validity stems precisely and primarily from the very fact that fossil resources are dwindling and becoming progressively more expensive. Furthermore, they are not a commonly shared richness, since their global distribution is totally uneven, which implies that certain countries are heavily dependent on others in this respect. These problems are of course affecting the energy outlook in the first instance, since some 95 per cent of the fossil resources are used as fuel, but the looming crisis will inevitably affect the corresponding chemical industry as well.

The purpose of this book is to show, through its attempt to cover, as exhaustively as possible, the wide spectrum of materials already potentially available, that renewable resources are perfectly apt to provide as rich variety of monomers and polymers as that currently available from petrochemistry. Implicit in this statement is the condition that substantial investments should be placed in the future to carry out the required research.

All contributors to this volume provided stimulating evidence about the potentials in their own field, but they are also aware that their efforts will turn into industrial realities only with the joint intervention of adequately financed fundamental and applied research, viz. the implication of both public and private sectors. If, on the one hand, it is encouraging to see a very impressive increase in this type of activity worldwide, the situation relative to petrochemistry, on the other hand, is still at a very low level of competitiveness. Qualitatively, a change in awareness has indeed taken place, parallel to the preoccupation surrounding the energy issues. This book is intended to amplify these promising initial stirrings by providing very sound examples of what can be achieved thanks to this alternative strategy.

Renewable resources are intrinsically valuable in this realm because of their ubiquitous character, which gives any society precious elements of sustainability, including with respect to polymeric materials. In all the topics covered by this book, emphasis is made, explicitly or implicitly, to the essential fact that the specific sources utilized for the purpose of producing new polymers, are taken neither from food, nor from natural materials, but instead from *by-products* of agricultural, forestry, husbandry and marine activities. One of the best examples of

this strategy is the production of furfural, since it can be carried out industrially virtually anywhere in the world (see Chapter 6), given the fact that any vegetable by-product containing pentoses represents an excellent raw material for its synthesis.

The term 'renewable resource', as used in this book, is defined as any animal or vegetable species which is exploited without endangering its survival and which is renewed by biological (short term) instead of geochemical (very long term) activities.

1.2   VEGETABLE RESOURCES

It is estimated that the world vegetable biomass amounts to about 10^{13} tons and that solar energy renews about 3 per cent of it per annum. Given its fundamental role in the maintenance of the oxygen level, the principle of sustainability limits its exploitation at most to that renewed percentage. With respect to the scope of this book, vegetable biomass can be divided into wood, annual plants and algae.

1.2.1   Wood

Wood is the most abundant representative of the vegetable realm and constitutes the paradigm of a composite material. It displays, on the one hand, a basic universal qualitative composition in terms of its major constituents (cellulose, lignin, hemicelluloses and polyphenols) and, on the other hand, species-specific components which can be polymeric, like poly-isoprene (natural rubber) and suberin, or small molecules, like terpenes, steroids, etc. An example of its morphology is shown in Fig. 1.1, which illustrates the role of the three basic components respectively as the matrix (lignin), the reinforcing elements (cellulose fibres) and the interfacial compatibilizer (hemicelluloses). The middle lamella (0.5–2 μm) is mainly composed of lignin (70 per cent), associated with small amounts of hemicelluloses, pectins and cellulose. The primary wall, often hard to distinguish from the middle lamella, is very thin (30–100 nm) and is composed of lignins (50 per cent), pectins and hemicelluloses. The secondary wall is the main part of the vegetal fibres. Its essential component is cellulose and it bears three layers, viz. the external, S_1 (100–200 nm), the central S_2 (the thickest layer of 0.5–8 μm) and the internal or tertiary layer, S_3 (70–100 nm) situated close to the lumen.

Wood is the structural aerial component of trees. The rest of their anatomy, namely roots, leaves, flowers and fruits, are not relevant to the aim of this book, and will therefore not be dealt with.

Cellulose dominates the wood composition, although its proportion with respect to the other main components can vary appreciably from species to species. Conversely, polyphenols are the least abundant components and moreover, can exhibit quite different structures. As for lignins and hemicelluloses, their relative abundance and their detailed structures are essentially determined by the wood family: softwoods are richer in lignins, whereas hardwoods are richer in hemicelluloses. These three basic polymeric components represent fundamental sources
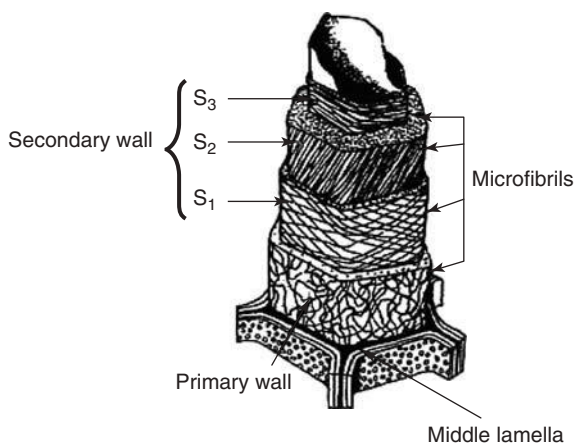
Figure 1.1   Typical morphology of a wood fibre.

of interesting materials and are thoroughly examined in this context, in specific chapters of this book, which focus their attention on the exploitation of these natural polymers after appropriate chemical treatment, with the aim of obtaining novel polymeric materials. The uses of wood itself as a structural material, as a source of furniture or flake boards and as a raw material in pulping, will not be treated here, because these applications call upon the exploitation of this fundamental natural resource through well-established technologies. Obviously, all these processes undergo regular improvement in their chemistry and engineering, but we deemed that their inclusion in the present treaty would have unduly overcharged its contents. The interested reader will find excellent monographs on each topic, going from introductory texts to highly specialized books [1–6].

The only area in which wood-related materials is witnessing important research contributions, concerns its physical and chemical modification, in order to protect it against degradation by various reagents or to obtain novel properties such as a thermoplastic behaviour. These aspects are treated in Chapter 20.

Similar considerations determined our decision not to include here chapters on the traditional uses of cellulose, like papermaking and cotton textiles, whose technologies are very thoroughly documented [7–10]. As for those cellulose derivatives which have been exploited for a very long time, like some cellulose esters and ethers, they will be dealt with in the appropriate chapter (Chapter 16), but again without a systematic treatment of the corresponding processes and properties [11–13].
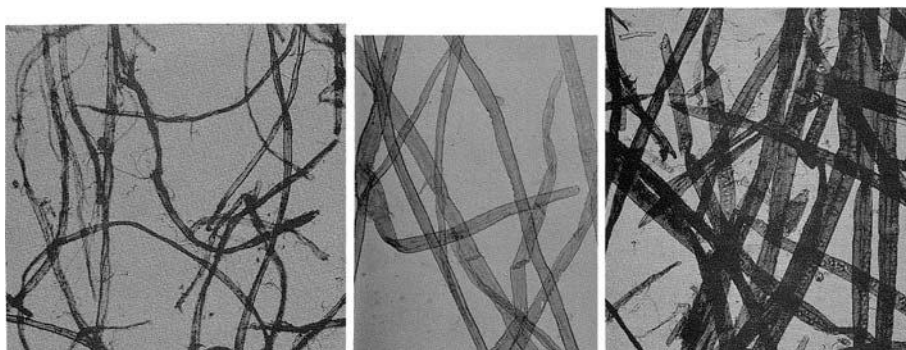
1.2.1.1   *Cellulose*

Virtually all the natural manifestations of cellulose are in the form of semi-crystalline fibres whose morphology and aspect ratio can vary greatly from species to species, as shown in Fig. 1.2. The subunits of each individual fibre are the microfibrils which in turn are made up of highly regular macromolecular strands bearing the cellobiose monomer unit, as shown in Fig. 1.3.

The interest of cellulose as a source of novel materials is reflected in this book through four chapters dealing, respectively, with (i) the chemical bulk modification for the preparation of original macromolecular derivatives with specific functional properties (Chapter 16); (ii) the surface modification of cellulose fibres in view of their use as reinforcing elements in composite materials and as high-tech components (Chapter 18); (iii) the processing and characterization of these composites, including the use of nano fibres (Chapter 19) and (iv) the technology and applications associated with bacterial cellulose (Chapter 17). These contributions clearly show that cellulose, the most abundant and historically the most thoroughly exploited natural polymer, still provides new stimulating avenues of valorization in materials science and technology.

1.2.1.2   *Lignins*

Lignin, the amorphous matrix of wood, is characterized by a highly irregular structure compared with that of cellulose, and is moreover known to vary considerably as a function of wood family (*in situ*) and of the isolation process, which always involves a depolymerization mechanism. Figure 1.4 gives a typical example of the structure of a lignin macromolecule with its most characteristic building blocks. The pulping technology which calls upon a delignification mechanism based on the use of sulphites, yields lignin fragments bearing sulphonate moieties (*i.e.* polyelectrolytes).

**Figure 1.2**   Cotton, pine and fir fibres.
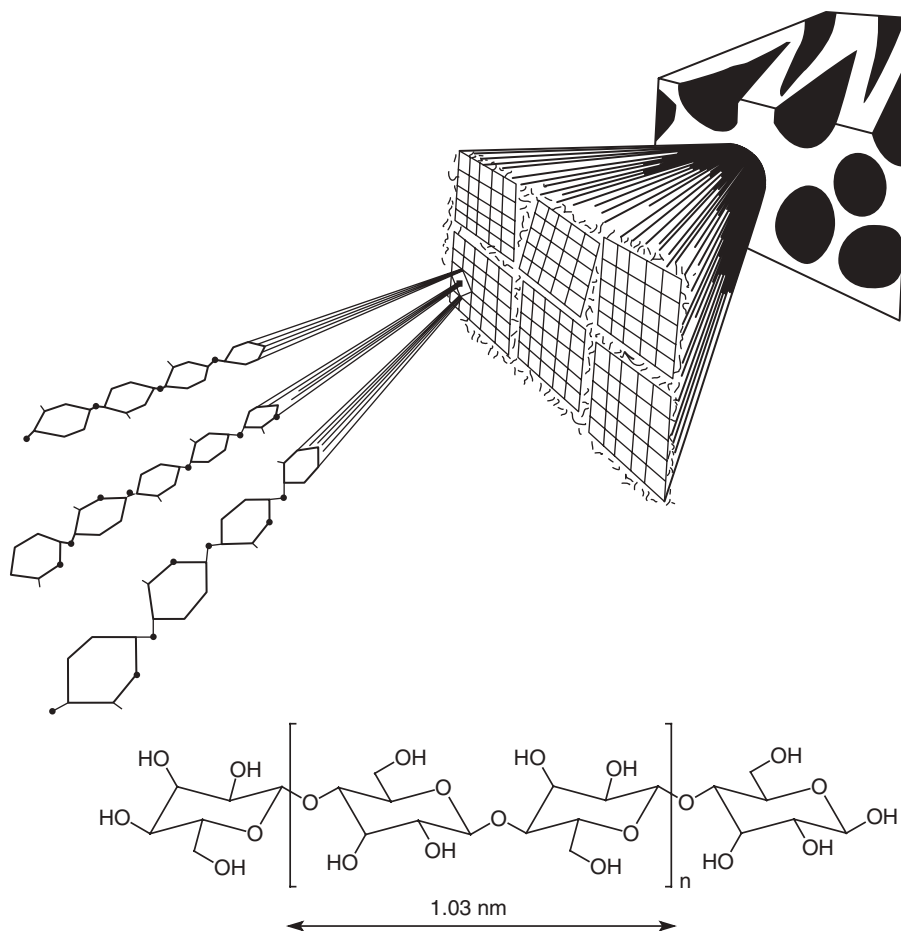
Figure 1.3   Schematic view of the components of cellulose fibre.

Traditionally, the aim of separating the wood components has been associated with papermaking, in which delignification isolates the cellulose fibres. In this context, the dissolved lignins have been utilized as fuel, which provides not only the energy required by the process, but also a convenient way of recovering its inorganic catalysts.

The idea of using these lignin fragments as macromonomers for the synthesis of polymers, by introducing them into formaldehyde-based wood resins, or by exploiting their ubiquitous aliphatic and phenolic hydroxyl groups, began to be explored only in the last quarter of the twentieth century. Given the fact that these industrial oligomers are produced in colossal amounts, it seems reasonable to envisage that a small proportion could be isolated for the purpose of producing new polymers, without affecting their basic use as fuel. Additionally, novel papermaking technologies, like the organosolv processes and biomass refinery approaches, like steam explosion, provide lignin fragments without the need of their use as a source of energy and with more accessible structures, in terms of lower molecular weights and higher solubility. Therefore, lignin macromonomers represent today a particularly promising source of novel materials based on renewable resources.

Three chapters are entirely devoted to lignin, covering (i) sources, structure and properties (Chapter 9), (ii) industrial processes and applications (Chapter 10) and (iii) their physical or chemical incorporation into novel macromolecular materials (Chapter 11). Moreover, its oxypropylation and the interest of the ensuing polyols are discussed in Chapter 12 and the properties of lignosulphonates as polyelectrolytes are dealt with in Chapter 24.
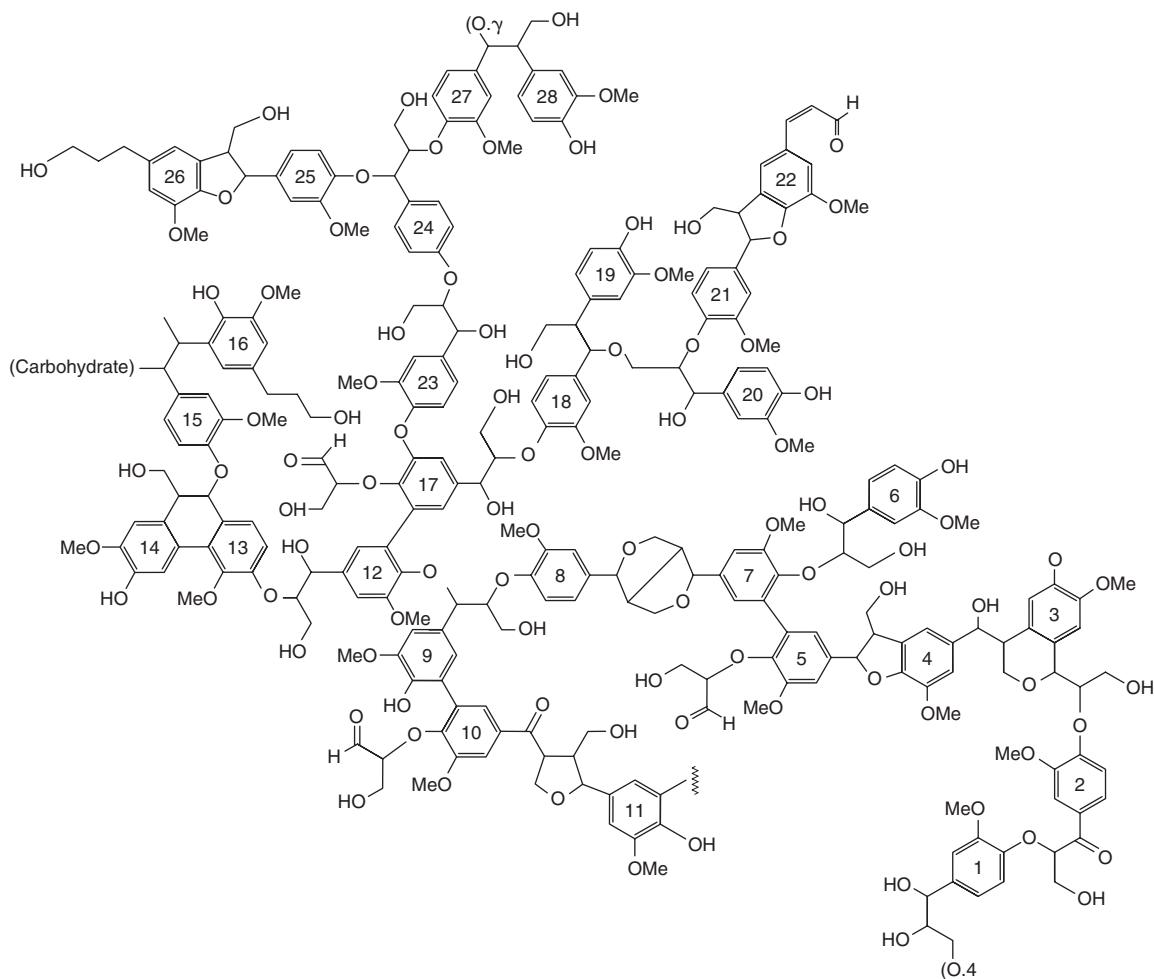
Figure 1.4   Lignin main moieties in a typical macromolecular assembly.
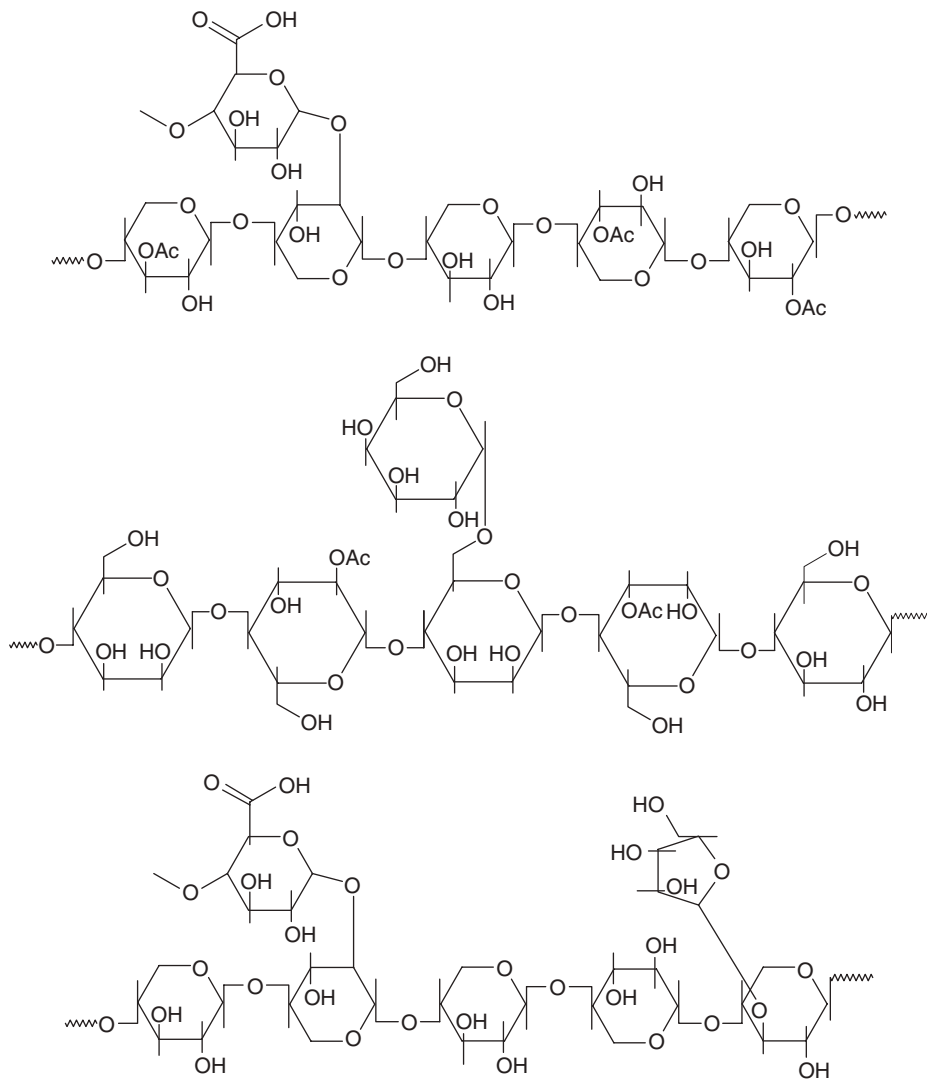
1.2.1.3   Hemicelluloses

Wood hemicelluloses are polysaccharides characterized by a relative macromolecular irregularity, compared with the structure of cellulose, both in terms of the presence of more than one monomer unit and by the possibility of chain branching. Figure 1.5 gives typical examples of such structures.

In papermaking processes, part of the wood hemicelluloses remain associated with the cellulose fibres, which results in the improvement of certain properties of the final material. The rest of these polysaccharides is dissolved together with lignin and in most processes it is burned with it. In some instances, however, particularly in the case of organosolv pulping or steam explosion technologies, the hemicelluloses can be recuperated as such. The utilization of wood hemicelluloses, but also of counterparts extracted from annual plants, has interested several industrial sectors for a long time, in particular that of food additives. In recent years, new possible outlets for hemicelluloses have been and are being explored, as discussed in Chapter 13.

1.2.1.4   Natural rubber

Turning now to more species-specific components, natural rubber is certainly one of the most important representatives. Different tropical trees produce different forms of poly(1,4-isoprene), which are exuded or extracted as an aqueous emulsion (latex) or as a sap-like dispersion, before coagulation. The *cis*-form of the polymer (Fig. 1.6(a)) tends to be amorphous and has a glass transition temperature of about −70°C, which makes it ideally suitable for application

Figure 1.5 Three typical hemicellulose structures.
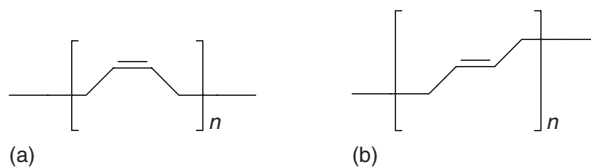
Figure 1.6 The two main structures of poly(1,4-isoprene) in natural rubber: (a) the *cis*-form and (b) the *trans*-form.

as elastomers, following chemical crosslinking (vulcanization) which involves some of its C=C insaturations. Its world production in 2004 was estimated at about 8 million tons. The *trans*-form (Fig. 1.6(b)), called *gutta percha* or balata, readily crystallizes forming rigid materials melting at about 70°C. As in the case of papermaking and cotton textile, the extraction and processing technology of these valuable natural polymers, as well as the preparation and optimization of their corresponding materials, represent a well-established and well-documented know-how [14] and is therefore not treated in this book. Examples of interesting recent contributions to the biosynthesis [15]
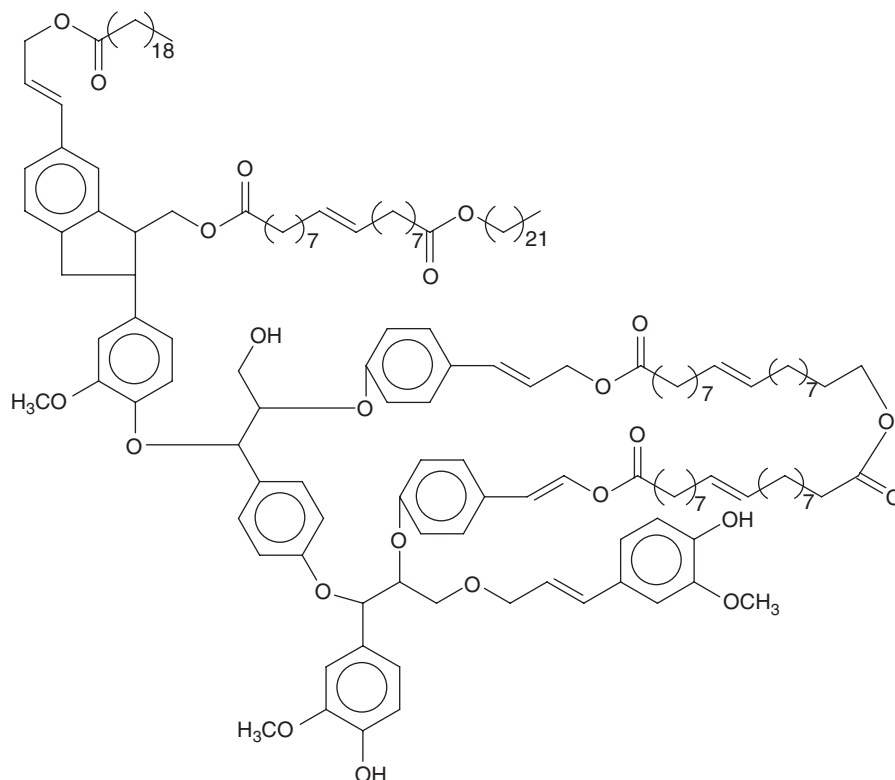
Figure 1.7   A schematic representation of the structure of suberin.

and chemical modification [16–18] of natural rubber are available. Moreover, the use of natural rubber in blends with other biopolymers like starch and lignins are discussed in the corresponding chapters.

1.2.1.5   Suberin

The other macromolecule found only in certain wood species is suberin. This non-linear polyester contains very long aliphatic moieties which impart a characteristic hydrophobic feature to the natural material that contains it. Figure 1.7 shows a schematic structure of suberin. By far the most representative species containing this polymer in its very thick bark (the well-known cork) is *Quercus suber*, which grows in the Mediterranean area, but Nordic woods like birch, also have a thin film of suberin coating their trunks. The sources of suberin, as well as the corresponding structure and composition are described in Chapter 14, together with the use of its monomeric components for the synthesis of novel macromolecular materials.

1.2.1.6   Tannins

Among the polyphenols present in the tree barks, tannins are by far the most interesting oligomers (molecular weights of 1 000–4 000) in terms of their utilization as macromonomers for the crosslinking of proteins in leather (tanning) and for macromolecular syntheses. The two representative structures of the flavonoid units in tannins are shown in Fig. 1.8. The most salient aspects related to the sources, structures and production of tannins and to their exploitation in polymer modification and manufacture are given in Chapter 8.
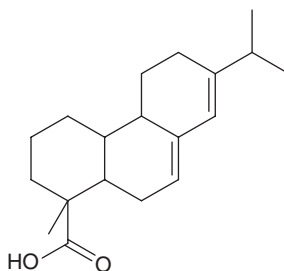
1.2.1.7   Wood resins

A number of resinous materials are secreted by trees. Their molecular weights are low (a few hundreds to a few thousands), hence a low melt viscosity, but their glass transition temperature can be as high as 100°C. Rosins (extracted
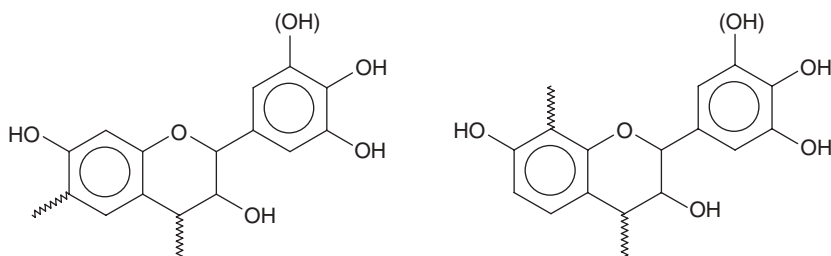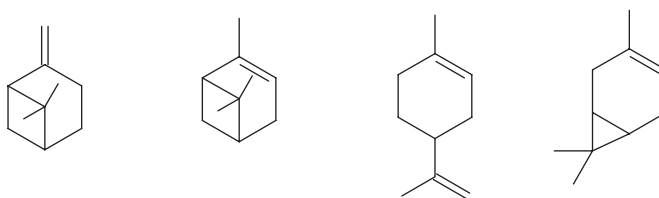
Figure 1.8   Two typical monomer units found in tannins.

Figure 1.9   Abietic acid.

Figure 1.10   Four common terpenes.

from pine trees) are the most important representative of this family. They are made up of a mixture of unsaturated polycyclic carboxylic acids of which, abietic acid (Fig. 1.9) is the major representative. A detailed description of the sources, extraction, structures and chemical modification of these substances is given in Chapter 4, together with their use as sources of polymeric materials.

1.2.1.8   *Terpenes*

Apart from all these natural polymers and oligomers, either general or specific wood components, certain trees also produce monomers in the form of terpenes which are unsaturated cyclic hydrocarbons of general formula $(C_5H_8)_n$, with *n* mostly equal to 2. Figure 1.10 shows typical representatives of such compounds. Chapter 2 is devoted to the description of the sources of these monomers, their relative abundance and their polymerization.

Numerous other interesting molecules are found in the different elements of the tree anatomy, which find specific uses as a function of their structure (*e.g.* as medicines, cosmetics, dyestuffs, etc.), but which are not exploitable in polymer synthesis. These valuable compounds have been the object of much (still ongoing) research and development [19] which falls outside the scope of this book.

1.2.2   Annual plants

The term annual plant is used here to define plants and crops with a typical yearly turnover, but includes also species with shorter or longer cycles. The primary interest of annual plants, which have been optimized by human

selection throughout the ages, is the production of food. Nevertheless, man has also exploited their residues for different purposes, including shelter, clothing, etc. In a complementary vein, annual plants have also been grown for the production of medicines, dyestuffs and cosmetics. In the framework of this book, attention will be focused on two different types of raw material, namely the fibrous morphologies of their basic structure and the substances they produce. Concerning the former, the lignocellulosic fibres of most plant stems fall into the same category as their wood counterpart and will therefore be discussed in the chapters devoted to cellulose. As for cotton (*i.e.* pure cellulose fibres annually produced by the corresponding plants) its traditional uses in textile, pharmaceutical aids, etc. reflect well-established and well-documented technologies, with little relevance to the primary scope of this book, as already pointed out in the case of papermaking and natural rubber technologies.

The relevant contribution of the output of annual plants to the realm of polymer synthesis and applications stems, instead, from some specific products, namely starch as a polymer, vegetable oils as triglyceride oligomers and hemicelluloses and monosaccharides as potential monomers or precursors to furan derivatives.

1.2.2.1   Starch

Starch is an extremely abundant edible polysaccharide present in a wide variety of tubers and cereal grains. In most of its manifestations, it is composed of two macromolecules bearing the same structural units, 1,4-*D*-glucopyranose, in linear (amylose, Fig. 11(a)) and highly branched architectures (amylopectin, Fig. 11(b)), present in different proportions according to the species that produces it. The utilization of starch or its derivatives for the production
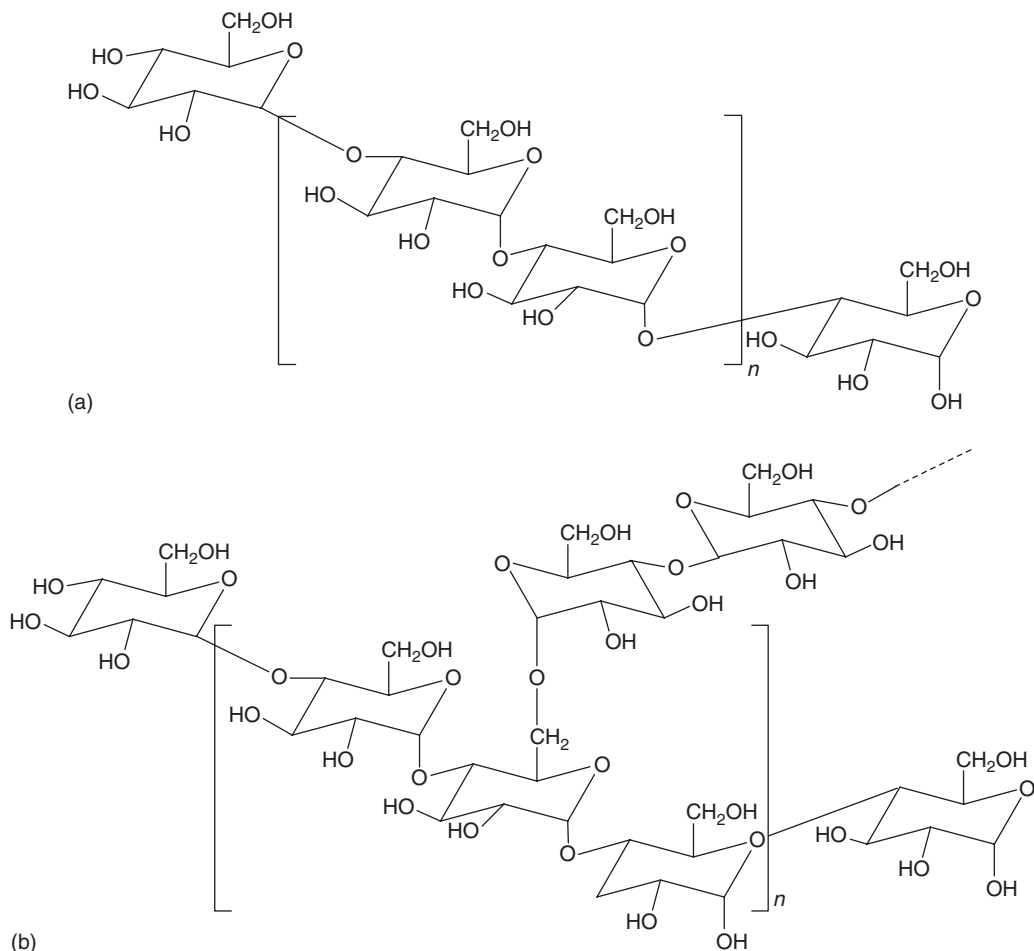
Figure 1.11   The two macromolecular components of starch: (a) amylose and (b) amylopectin.

of adhesives, or as wet-end additives in papermaking, constitute traditional applications to which a variety of novel materials, including plasticized starch, blends and composites, have been recently added, as discussed in Chapter 15.

1.2.2.2 Vegetable oils

Vegetable triglycerides are among the first renewable resources exploited by man primarily in coating applications ('drying oils'), because their unsaturated varieties polymerize as thin films in the presence of atmospheric oxygen. This property has been exploited empirically for millennia and has received much scientific and technological attention in the last few decades. These oils are extracted from the seeds or fruits of a variety of annual plants, mostly for human consumption. Within their general structure, consisting of glycerol esterified by three long-chain aliphatic acids (Fig. 1.12) bearing variable number of carbon atoms, the most relevant difference is undoubtedly the number of C=C insaturations borne by the chains, but other more peculiar features are also encountered (e.g. hydroxyl moieties). Their essential role as components of paints and inks constitute the most important application for the elaboration of materials. This traditional technology is presently being updated through research aimed at modifying the pristine structure of the oils in order to enhance their reactivity, particularly in the realm of photo-sensitive coatings, and thus render them competitive with respect to petroleum-based counterparts, like acrylic resins. Chapter 3 covers this reviving area of material science applied to renewable resources.

This chapter deals comprehensively with both triglycerides and fatty acids as sources of novel polymeric materials, but does not cover the growing interest in glycerol and its chemical transformation into other useful chemicals. This topic has been recently reviewed [20–22] and Chapter 7 discusses the interest of glycerol in the synthesis of surfactants derived from triglycerides.

1.2.2.3 Hemicelluloses

Annual plants produce a rich selection of hemicelluloses, often with quite different structures compared with those found in woods, although of course the basic chemical features are always those of polysaccharides. It follows that specific applications are associated with these different structural features, notably as food additives. The presence of charged monomer units is one of the most exploited characteristics, because of the ensuing rheological sensitivity to physical parameters. The properties and applications of plant and seaweed hemicelluloses are dealt with in Chapters 13 and 24, the latter dealing with the specific features related to polyelectrolytes.

In a different vein, plants rich in C5 hemicelluloses and more specifically xylans, are excellent raw materials for the production of furfural (Fig. 1.13). This simple technology, developed more than a century ago, has been applied to
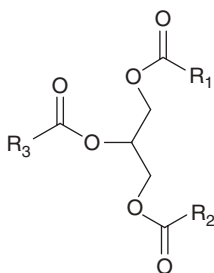
Where R_1, R_2 and R_3 are fatty acid chains.

Figure 1.12   The basic structure of triglycerides.
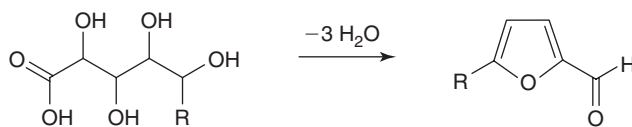
R = H (furfural) or CH_3 (5-methyl furfural)

Figure 1.13   Schematic conversion of aldopentoses into furfural and 5-methyl furfural.

a whole host of annual plant residues, after the extraction of their food component, ranging from corn cobs, rice halls and sugar cane bagasse to olive husks. The industrial production of furfural is therefore possible in any country and indeed implemented in many of them, because of the wide variety of biomass containing its precursor and represents a beautiful example of the exploitation of renewable resources using a readily implemented and cheap process.

The use of furfural as such, as well as its transformation into a variety of furan monomers is discussed in Chapter 6 together with the synthesis and properties of the corresponding macromolecular materials.

Another possible exploitation of annual plant residues, after the separation of their foodstuff, is their conversion into polyols by oxypropylation. In this context, the whole of the residue is involved in the transformation, providing a convenient and ecological source of macromonomers. A typical example of this strategy is described in Chapter 12, in the case of sugar beet pulp, which is poor in xylans and cannot therefore be considered as a possible source of furfural.

1.2.2.4   *Mono and disaccharides*

The traditional use of some of the most important mono and disaccharides as sweeteners, whether energetic or not, is of course outside the scope of this book. The interest in using this family of compounds, produced by different annual plants, as precursors to novel materials, has increased considerably in recent years, mostly in three different directions, viz. (i) the conversion of fructose to hydroxymethyl furfural (Fig. 1.14), (ii) the synthesis of polycondensation materials using sugars as comonomers and (iii) the preparation of surfactants based on renewable resources.

Hydroxymethyl furfural is the other first generation furan derivative readily obtained from hexoses (C6 saccharides) [22]. Its role as a precursor to a large spectrum of monomers and the interest of the ensuing polymers constitute the topics of Chapter 6, complementary to those relative to furfural.

The synthesis of novel polymers, mostly polyesters and polyurethanes, based on mono and disaccharides (Fig. 1.15), together with their properties and possible applications, are described in Chapter 5.

A large section of Chapter 7 is devoted to the preparation of green surfactants based on sugars (Fig. 1.16). The inclusion of the topic of surfactants from renewable resources in this book stems from the fact that these compounds can play decisive roles in the synthesis, the processing and the application of polymers and must therefore be considered as an integral part of polymer science and technology.
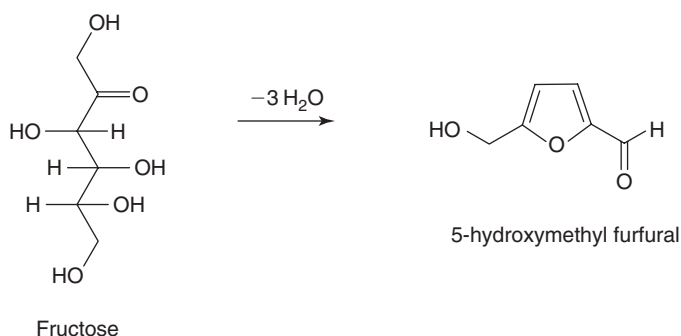
Figure 1.14   Schematic conversion of fructose into 5-hydroxymethyl furfural.
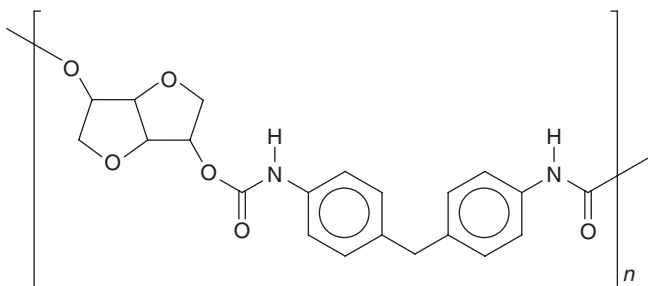
Figure 1.15   A sugar-based polyurethane.
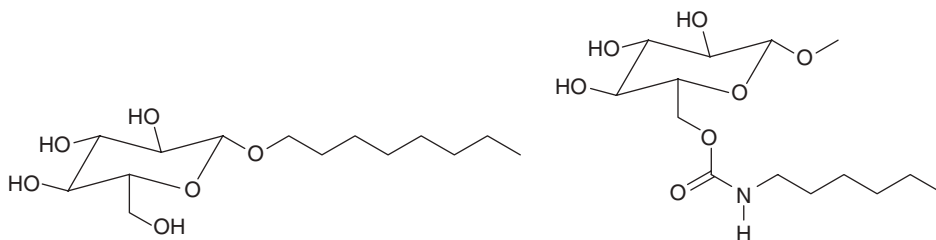
Figure 1.16　Two sugar-based non-ionic surfactants.

The fermentation of glucose has opened new avenues in the synthesis of polymers derived from renewable resources, with particular emphasis on the exploitation of lactic acid as a monomer. This topic is dealt with in Chapter 21.

1.2.3　Algae

Marine biomass is also a very interesting source of precursors to materials, both in terms of vegetable and animal resources. Polysaccharides derived from certain algae, like alginates, have been exploited for a long time as polyelectrolyte materials. This family of polymers are included in the contents of Chapter 24.

1.3　ANIMAL RESOURCES

As in the case of vegetable resources, all the traditional technologies of exploitation of materials derived from the animal realm will not receive a detailed treatment in this book. Thus, readers interested in leather [23], wool [24], silk [25], gelatin [26], animal fats and waxes [27] and carbon black [28], as well as animal-based resins like shellac [29], are invited to consult the corresponding monographs quoted here. The reason for these exclusions stems from the fact that the processes associated with the production of these materials have not been the object of any major qualitative improvement in recent times.

1.3.1　Chitin and chitosan

Chitin is undoubtedly the most abundant animal polysaccharide on earth. It constitutes the basic element of the *exo*-skeleton of insects and crustaceans, but it is also found in the outer skin of *fungi*. Chitin is a regular linear polymer whose structure differs from that of cellulose by the presence of *N*-methylamide moieties instead of the hydroxyl groups at C2 (Fig. 1.17). Given the susceptibility of this function to hydrolysis, chitin often bears a small fraction of monomer units in the form of primary amino groups resulting from that chemical modification.

Chitin is sparingly soluble even in very polar solvents, because of its high cohesive energy associated with strong intermolecular hydrogen bonds (NH—CO), which is also the cause of its lack of melting, because the temperature at which this phase change would occur is higher than that of the onset of its chemical degradation, just like with cellulose. It follows that the potential uses of chitin are strongly limited by these obstacles to processing. The possibility of exploiting chitin is therefore dependent on its transformation into its deacetylated derivatives through hydrolysis. As the proportion of the amide function converted into primary amino groups increases along the macromolecule, the
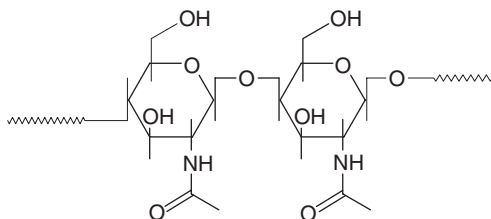
Figure 1.17　Chitin.
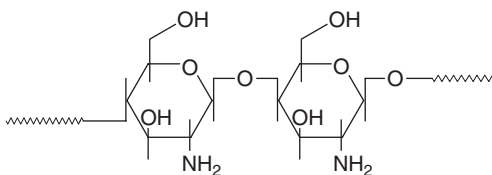
Figure 1.18   The main monomer units in chitosan.

corresponding material becomes progressively more soluble in such simple media as week aqueous acids or polar protic solvents. The ideal fully hydrolysed polymer takes the name of chitosan (Fig. 1.18), a term which is in fact also attributed to all random copolymers bearing more than about 50 per cent of amino monomer units.

Chitosan has become one of the most attractive polymers derived from renewable resources, because it possesses remarkable properties which find applications in many areas of material science and technology, particularly related to biomaterials and medical aids. It is not exaggerated to talk about the boom of chitosan-related research, considering the explosion of scientific and technical literature on this polymer, accompanied by the creation of learned societies and the frequent international meetings covering its progress. Industrial units devoted to the extraction of chitin followed by the production of chitosan are springing up throughout the world. The materials derived from chitin and chitosan are described in Chapter 25.

1.3.2   Proteins

Because of their highly polar and reactive macromolecular structure, proteins have attracted much attention in the last few decades, as possible sources of novel polymeric materials. The details of this activity are discussed in Chapter 23. A particularly interesting natural proteinic material is undoubtedly the spider dragline silk, because of its extraordinary mechanical properties. Given the obvious difficulties related to gathering viable amounts of this biopolymer, much research is being devoted to its bioengineering production [30].

### 1.3.3   Cellulose whiskers from molluscs

Although cellulose is the supreme example of a *predominantly vegetable* natural polymer, exotic animal species are known to produce this polysaccharide and, more particularly, some of its most regular manifestations. Thus, the tunicate mollusc has became the very symbol associated with cellulose whiskers (*i.e.* extremely regular nanorods with remarkable mechanical and rheo-modifying properties) as described in Chapter 19.

1.4   BACTERIAL POLYMERS

Although the polymerization induced by bacteria has been known and studied for a long time, the strategy based on using this biological activity to actually harvest commercial materials is a relatively recent endeavour. Two specific instances are prominent in this context, namely the production of poly(hydroxyalkanoates) and the synthesis of bacterial cellulose.

1.4.1   Poly(hydroxyalkanoates)

This family of polyesters and copolyesters (Fig. 1.19) has interested the polymer community both because of their remarkable physical properties and biodegradability. Efforts have been actively implemented to improve the economy of the biotechnological processes used to prepare these materials, so that they can become commercially competitive compared with petroleum-based polymers with similar properties. All these aspects are thoroughly tackled in Chapter 22.
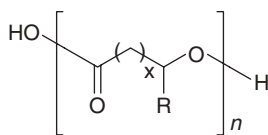
Figure 1.19 The general formula of poly(hydroxyalkanoates).
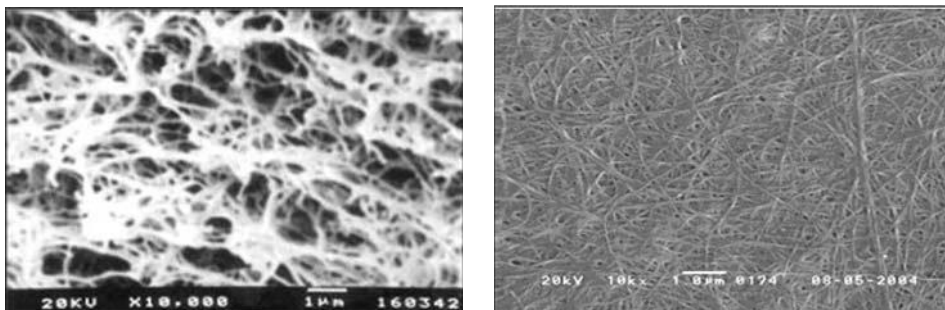
Figure 1.20 The unique morphology of bacterial cellulose.

1.4.2 Bacterial cellulose

Although the chemical structure of bacterial cellulose is identical to that of any other vegetable-based counterpart, its fibrous morphology (Fig. 1.20), as obtained directly in its biotechnological production, is unique and consequently the properties associated with this original material are also peculiar and promise very interesting applications. Details about this futuristic biopolymer are given in Chapter 17.

1.5 CONCLUSIONS

This book is not the first survey dealing with the interest of natural polymers or materials derived from renewable resources, since several monographs have been published in recent years [31–40], including two excellent reviews by Corma *et al*. covering the transformation of biomass for the production of fuel [41] and chemicals [21] and other recent contributions [42, 43]. The concept of the biorefinery [31, 44] is explicitly or implicitly at the basis of all these treaties, that is, the working hypothesis proposing a rational separation and exploitation of all the components of a given natural resource. The other common denominator to many of these collective overviews is the biodegradable character of the ensuing material.

We have attempted to gather in the present volume what we feel is a more comprehensive collection of monographs, with the materials science elements as the predominant feature. Of course, both the biorefinery and the biodegradability issues remain essential here, but within the primary focus spelled out in the title (*i.e.* ultimately the production of macromolecular materials from renewable resources).

REFERENCES

1. Fengel D., Wegener G., *Wood Chemistry Ultrastructure Reactions*, Walter de Gruyter, Berlin, 1989; Kennedy J.F., Philips, G.O., Williams P.A., *The Chemistry and Processing of Wood and Plant Fibrous Materials*, Woodhead, Cambridge, UK, 1996.
2. Hill C.A.S., *Wood Modification: Chemical, Thermal and Other Processes*, John Wiley & Sons, Ltd, Chichester, 2006.
3. Kettunen, P.O., Wood: Structure and properties, Mater. Sci. Found., 2006, Trans Tech Publications Ltd., Uetikon-Zuerich, 2006, pp. 29–30.
4. Rowell R.M., *Handbook of Wood Chemistry and Wood Composites*, CRC Press, Boca Raton, 2005.
5. Gullichsen J., Paulapuro H., *Papermaking Science and Technology*, Fapet Oy, Helsinki, 1999, Volumes 2 and 3.

6.   Roberts J.C., *Paper Chemistry*, 2nd Edition, Chapman & Hall, United Kingdom, 1996; Eklund, D. Lindström, T., *Paper Chemistry: An Introduction*, DT Paper Science Publications, Grankulla, Finland, 1991.

7.   Casey J.P., *Pulp and Paper Chemistry and Chemical Technology*, 3rd Edition, John Wiley and Sons, New York, 1980, Volumes 1–4.

8.   Gullichsen J., Paulapuro H., *Papermaking Science and Technology*, Fapet Oy, Helsinki, 1999, Volumes 4–10.

9.   Wakelyn P.J., Bertoniere N.R., French A.D., Thibodeaux D.P., Triplett B.A., Rousselle M.A., Goynes W.R. Jr., Edwards J.V., Hunter L., McAlister D.D., Gamble G.R., *Cotton Fibre Chemistry and Technology*, CRC Press, Boca Raton, 2007.

10. Ash M., Ash I., *Handbook of Textile Processing Chemicals*, Synapse Information Resources, Endicott, New York, 2001; Horrocks A.R., Anand S.C., *Handbook of Technical Textiles*, Woodhead Publ., Cambridge, UK, 2000.

11. Heinze T., Liebert T., Koschella A., *Esterification of Polysaccharides*, Springer, Berlin, 2006.

12. Hon D.N.S., Shiraishi N., *Wood and Cellulosic Chemistry*, Marcel Dekker Inc., New York, 1992.

13. Goetze K., *Synthetic Fibers by the Viscose Process* Springer-Verlag, 1967; Burt T.P., Heathwaite A.L., Trudgill T.S., *Nitrate: Processes, Patterns and Management*, Wiley, Chichester, UK, 1993.

14. Brendan R., *Rubber Compounding: Chemistry and Applications*, Marcel Dekker Inc., New York, 2004; Parry D.A.D., Squire J.M., Fibrous proteins: Coiled-coils, collagen and elastomers, *Adv. Protein Chem.*, **70**, 2005, Elsevier, San Diego, 2005.

15. Puskas J.E., Gautriaud E., Deffieux A., Kennedy J.P., *Prog. Polym. Sci.*, **31**, 2006, 533.

16. Kawahara S., Saito T., *J. Polym. Sci., Part A: Polym. Chem.*, **44**, 2006, 1561.

17. Kangwansupamonkon W., Gilbert R.G., Kiatkamjornwong S., *Macromol. Chem. Phys.*, **206**, 2005, 2450.

18. Jacob M., Francis B., Varughese K.T., Thomas S., *Macromol. Mater. Eng.*, **291**, 2006, 1119.

19. Murzin D.Y., Maki-Arvela P., Salmi T., Holmbom B., *Chem. Eng. Technol.*, **30**, 2007, 569.

20. Pagliaro M., Ciriminna R., Kimura H., Rossi M., Della Pina C., *Angew. Chem. Int. Ed.*, **46**, 2007, 4434.

21. Corma A., Iborra S., Velty A., *Chem. Rev.*, **107**, 2007, 2411.

22. Chheda J.N., Huber G.W., Dumesic J.A., *Angew. Chem. Int. Ed.*, **46**, 2007, 7164; Behr A., Eilting J., Irawadi K., Leschinski J., Lindner F., *Green Chem.*, **10**, 2008, 13.

23. Bienkiewicz K.J., *Physical Chemistry of Leather Making*, Krieger, Melbourne, FL, 1983.

24. Simpson W.S., Crawshaw G.H., *Wool: Science and Technology*, Woodhead Publ., Cambridge, UK, 2002.

25. Scheibel T., Silk, Special Issue of *Appl. Phys. A: Mater. Sci. Process*., **82**, 2006, Springer, Heidelberg, 2006.

26. Schreiber R., Gareis H., *Gelatine Handbook*, Wiley-VCH, Weinheim, 2007.

27. Hamilton R.J., *Waxes: Chemistry, Molecular Biology and Functions*, The Oily Press, Dundee, UK 1995; Berger K.G., Animal Fats-BSE and After. *Proceedings of a Joint Meeting of the SCI Oils & Fats Group and the SCI Food Commodities & Ingredients Group*, London, UK, 10 June 1997, PJ Barnes & Associates, Bridgewater, UK, 1997.

28. Donnet J.B., Bansai R.C., Wang M.J., *Carbon Black: Science and Technology*, 2nd Edition, Marcel Dekker, New York, 1993.

29. Hicks E., *Shellac: Its Origin and Applications*, MacDonald, London, 1962.

30. Bini E., Po Foo C.W., Huang J., Karageorgiou V., Kitchel B., Kaplan D.L., *Biomacromolecules*, **7**, 2006, 3139.

31. Kamm B., Gruber P.R., Kamm M., *Biorefineries–Industrial Processes and Products*, Wiley VCH, Weinheim, 2006, Volumes 1 and 2.

32. Khemani K., C. Scholz, (Eds.), Degradable polymers and materials: Principles and practice, *ACS Symp. Ser.*, **939**, 2006, ACS, Washington DC.

33. Fingerman M., Nagabhushanam R., *Biomaterials from Aquatic and Terrestrial Organisms*, Science Publishers, Enfield, NH, 2006.

34. Im S.S., Kim Y.H., Yoon J.S., Chin I.J. (Eds), *Bio-Based Polymers: Recent Progress*, 2005, Wiley, New York.

35. Scott G., *Degradable Polymers, Principles and Applications*, 2nd Edition, Kluwer Academic, New York, 2003.

36. Steinbüchel A., Marchessault R.H., *Biopolymers for Medical and Pharmaceutical Applications*, Wiley, Weinheim, 2005.

37. Stevens C.V., Verhé R.G., *Renewable Bioresources: Scope and Modification for Non-Food Applications*, John Wiley & Sons, Ltd, Chichester, 2004.

38. Wool R.P., Sun X.S., *Bio-Based Polymers and Composites*, Elsevier, Amsterdam, 2005.

39. Wolf O., Techno-Economic Feasibility of Large-scale Production of Bio-Based Polymers in Europe, *Technical Report EUR 22103*, European Commission, 2005.

40. Argyropoulos D.S., (Ed.), Materials, chemicals and energy from forest biomass, *ACS Symp. Ser.*, **954**, 2007, ACS, Washington DC.

41. Huber G.W., Iborra S., Corma A., *Chem. Rev.*, **106**, 2006, 4044.

42. Gallezot P., *Green Chem.*, **9**, 2007, 295.

43. Darder M., Aranda P., Ruiz-Hitzky E., *Adv. Mater.*, **19**, 2007, 1309.

44. Sanders J., Scott E., Weusthuis R., Mooibroek H., *Macromol. Biosci.*, **7**, 2007, 105.

– 2 –

Terpenes: Major Sources, Properties and Applications

Armando J.D. Silvestre and Alessandro Gandini

ABSTRACT

Turpentine, the volatile fraction of the so-called Naval Stores Industry is a complex mixture, mainly composed of monoterpenes. This chapter begins with a general overview of the major sources of turpentine, its composition and classical applications, including a systematic layout of the structure of terpenes. This is followed by a detailed discussion of the use of α- and β-pinene and other monoterpenes as monomers in conventional free radical and cationic homopolymerizations and copolymerizations, the latter involving other terpenes, monoterpene alcohols or synthetic monomers. Finally, the living cationic and living radical homo- and co-polymerization of β-pinene are thoroughly examined in terms of mechanisms and macromolecular structures. Throughout, the properties and possible applications of the materials ensuing from each type of system are critically examined.

2.1   INTRODUCTION

The term 'terpenes' refers to one of the vastest families of naturally occurring compounds which bear a common biosynthetic pathway, but show enormous structural diversity depending on the number of carbon atoms (normally multiples of five), the variety of possible biosynthetic isomeric carbon skeletons and the stereochemical configurations.

Terpenes are secondary metabolites synthesized mainly by plants, but also by a limited number of insects, marine micro-organisms and fungi. These compounds were first considered as 'waste' products from plant metabolism with no specific biological role, but later, the involvement of some terpenes as intermediates in relevant biosynthetic processes was discovered [1]. Additionally, it has been well demonstrated that many terpenes play important ecological roles [1] as in plant defence, for example as insect repellents, and in symbiotic mechanisms, for example as attractants to specific insect species to stimulate cross pollination.

Most terpenes share isoprene (2-methyl-1,4-butadiene) as a common carbon skeleton building block. This structural relationship was identified by Wallach in 1887, who recognized that most terpenic structures result from the 'head-to-tail' condensation of isoprene units and this became known as the 'isoprene rule'. Based on this generic rule, terpenes can be classified according to the number of isoprene units (Table 2.1).

In the 1950s, Ruzicka proposed the 'biogenic isoprene rule' which states that all terpenes can be obtained by condensation, cyclization and/or rearrangement of a defined number of precursors sharing a common biosynthetic pathway [2]. The key precursor for monoterpenes is geranyl pyrophosphate, which, upon elimination of the pyrophosphate moiety, forms a *p*-menthane-type carbenium ion. Most common monoterpene skeletons are then derived from this carbocation through several rearrangement steps (Fig. 2.1).

Table 2.1

Major groups of terpene compounds
according to the number of isoprenic units

Classification	Isoprene units
Hemiterpenes	1
Monoterpenes	2
Sesquiterpenes	3
Diterpenes	4
Sesterpenes	5
Triterpenes	6
Tetraterpenes	8
Polyterpenes	n
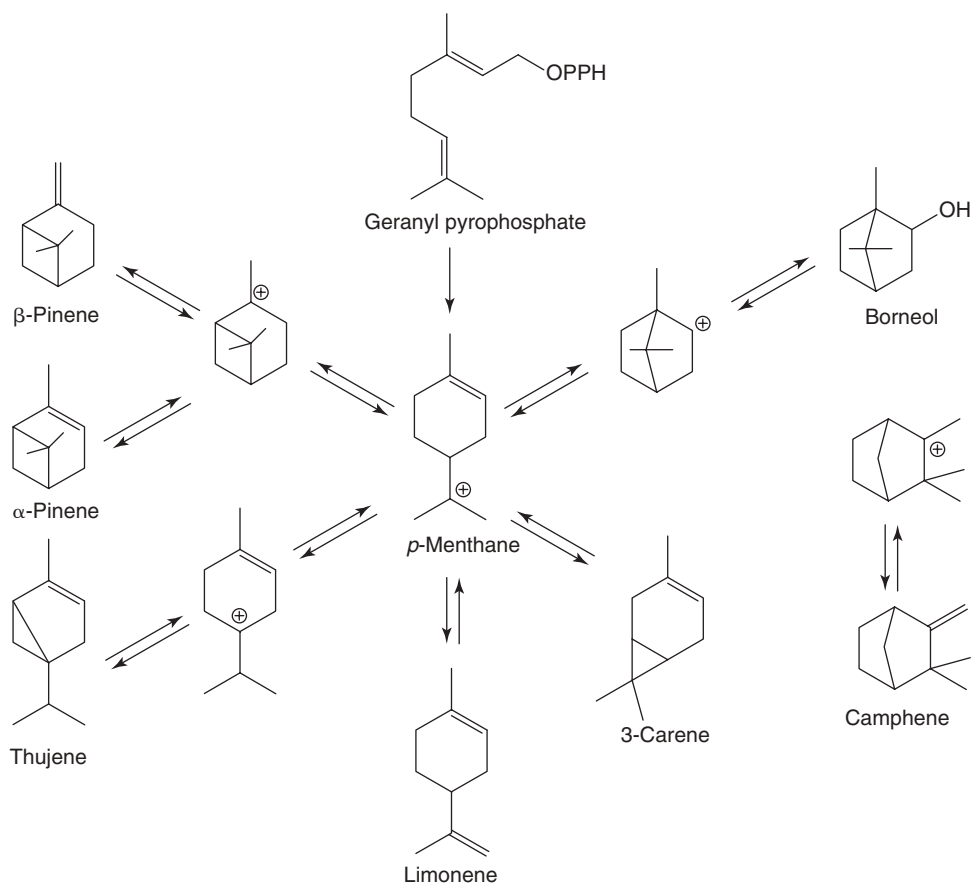
Figure 2.1   General outline of the biosynthetic pathway to the formation of main monoterpene skeletons.

Monoterpenes are extraordinarily diverse not only because of the variety of their basic skeletons, but also because a large number of stereoisomers are possible given the presence of stereogenic centres in every skeleton, and because of the wide variety of oxygenated derivatives (alcohols, aldehydes, ketones and carboxylic acids) that can be derived from those basic skeletons.

An important feature of monoterpenes (obvious from Fig. 2.1) is the ease with which the basic skeletons can interconvert to give rise to any monoterpene (or its derivatives) starting from any abundant precursor. This is one of the main reasons why pine turpentine has been used for decades as the most important source of terpenes in a vast number of industrial applications.

The systematic study of monoterpene chemistry started in the late 19th century, although their use as naturally occurring oils, known as 'essential oils', is a millenary activity. Thus for example, α-pinene rich oils were used as solvents by ancient Egyptians and Persians; menthol was used in Japanese medicine 2000 years ago and the medicinal use of camphor was reported as early as the 11th century [1]. The 'essential oil' designation finds its origin in the work of Paracelsus (15th century), who named the active principle of any medicinal substance as *quinta essentia*, and it is now used to designate the volatile terpenic fractions (mainly mono and sesquiterpenes) isolated from plants. Finally, these compounds were called terpenes by Kekulé, when he first identified terpene structures isolated from 'turpentine oil' extracted from *Pistacia therebinthus* L. Essential oils are predominantly composed of monoterpenes with a smaller fraction of sesquiterpenes. They find a very wide range of applications in cosmetics and pharmaceuticals [3, 4], insecticides [5], polymers [6] and other areas [1, 7].

Considering the aim of this book, only brief mentions will be given to applications other than polymeric materials and the discussion will be focused on turpentine, the main source of monoterpenes used as precursors for polymeric materials.

2.2 TURPENTINE

Turpentine is the common term given to the volatile fraction isolated from pine resin. For historical reasons, pine resin was called 'Naval Stores', due to its widespread use in the waterproofing of wooden ships. Depending on the way pine resin is isolated from wood, three products are distinguished viz. gum naval stores, obtained from tapping living trees; sulphate naval stores, recovered during the kraft pulping of pine wood (also known as tall oil resin) and wood naval stores, obtained from the solvent extraction of wood after harvesting. Details on the origin, extraction and purification of turpentine have been discussed in detail in the classic treatise Naval Stores by Zinkel and Russel [8].

Turpentine is by far the most widely produced essential oil in the world and consequently the privileged source for applications requiring large-scale supplies. The total world turpentine production showed a tendency to decline between the 1960s and the 1980s. However, statistics covering the next decade [9, 10] show that the turpentine production stabilized around 330 000 tons per year, with 70 per cent of the world production as sulphate turpentine, and the rest almost exclusively as gum turpentine [10, 11].

The turpentine chemical composition is strongly dependent on the tree species and age, geographic location and the overall procedure used to isolate it. In general, however, the major components are a few unsaturated hydrocarbon monoterpenes ($C_{10}H_{16}$) namely, α-pinene (45–97 per cent) and β-pinene (0.5–28 per cent) with smaller amounts of other monoterpenes (Fig. 2.2) [12].
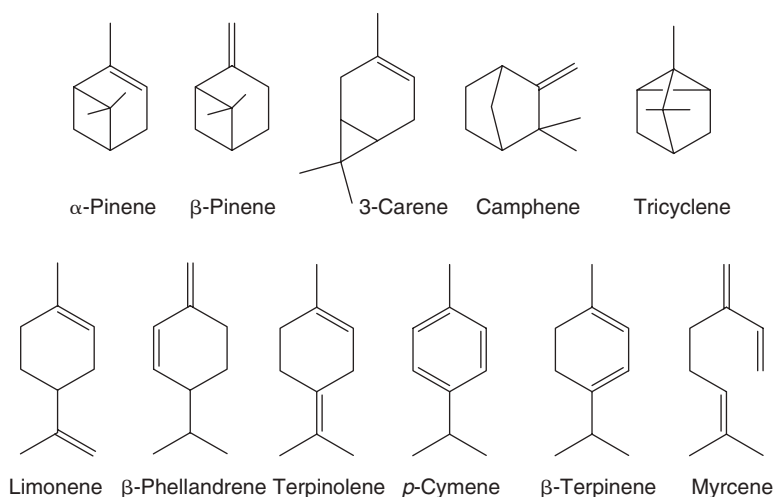
Figure 2.2   Chemical structures of the most common turpentine monoterpene components.

   Turpentine was mainly used as a solvent in the 1940s (*ca.* 95 per cent) and only a minor fraction was exploited as a raw material for the chemical industry (*ca.* 5 per cent). Because of the progressive exploitation of the peculiar reactivity of its terpenic components [1, 12], these figures were completely reversed in the 1980s, with at least 95 per cent of the turpentine production being employed as Q reagent for the chemical industry [11, 13]. Historically, the most relevant uses of turpentine components as reagents include insecticides, although this application was progressively banned from the 1970s [5], pine oil production [7], flavours and fragrances and other fine chemicals [3, 4] as well as polyterpene resins [6, 13]. According to statistics related to the 1980–1990 decade, of the latter three applications, pine oil production dominated the turpentine use with 50 per cent, while the other two sectors used 25 per cent each.

   Before dealing with the major topic of this chapter, that is, polymer synthesis, a brief overview of other turpentine applications is given in the following section.


2.3   TURPENTINE APPLICATIONS

### 2.3.1   Insecticides from turpentine

As mentioned above, the application of turpentine in the insecticide industrial production is no longer relevant [5], notably in the case of Thanite (isobornyl thiocianoacetate) and Toxaphene (a very complex mixture of chlorinated derivatives with an average empirical formula of $C_{10}H_{10}Cl_8$), both prepared from camphene (Fig. 2.3).

2.3.2   Synthetic pine oil from turpentine

Synthetic pine oil is prepared by the hydration of α-pinene with aqueous mineral acids (Fig. 2.4), and is mainly used in household cleaning and disinfection products [7]. The acidic conditions promote the formation of an intermediate carbocation which readily undergoes rearrangement to form predominantly the isomeric *p*-menthane carbocation, followed by water addition to generate essentially α-terpineol (Fig. 2.4) and minor amounts of fenchol and borneol.
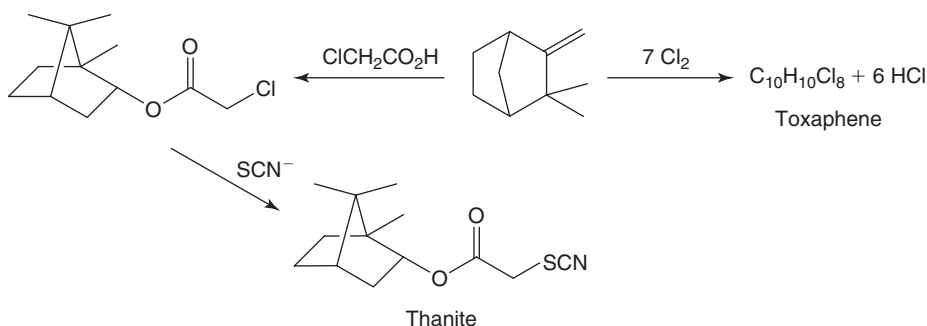
Figure 2.3   Examples of insecticides prepared from turpentine components.
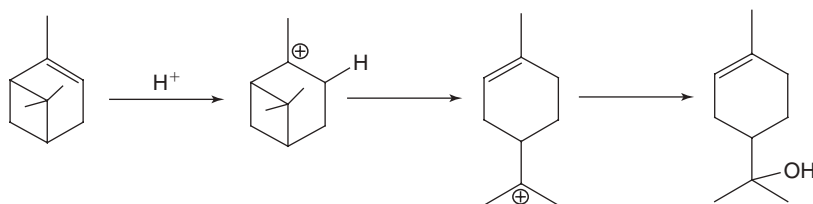
Figure 2.4   Conversion of α-pinene into synthetic pine oil.
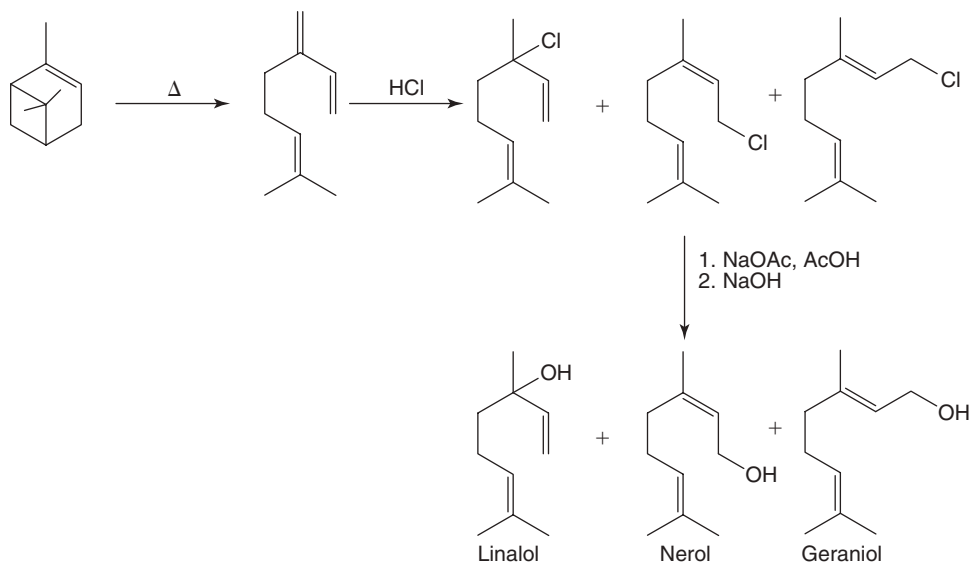
Figure 2.5   Synthesis of linalol, nerol and geraniol.

2.3.3   Flavours and fragrances from turpentine

The use of turpentine in the production of flavours and fragrances and other fine chemicals for bulk commodities mainly takes advantage of the thermal or acidic isomerization of the abundant α- and/or β-pinenes to produce the molecular skeletons of many naturally occurring fragrant chemicals (particularly when their natural sources are not abundant) and a wide variety of other fine chemicals [1, 3, 4].

Among the vast number of applications, an important example is the production of the so-called rose alcohols from β-pinene, viz. nerol, geraniol and linalool, key intermediates in the synthesis of many major fragrances. This process involves the thermal isomerization to myrcene, followed by addition of HCl, substitution by acetate and alkaline hydrolysis, as shown in Fig. 2.5 [3].

Apart from their applications as widespread fragrant raw materials, these terpenic alcohols, together with α-terpineol, have also attracted some interest in recent years as comonomers for radical copolymerization, as discussed later (Section 2.4.4.3).

Pinenes have also been used as feedstock to prepare several linear non-conjugated non-terpenic dienes (*e.g.* 3,7-dimethyl-1,6-octa-1,6-diene and 5,7-dimethylocta-1,6-diene) used in the synthesis of elastomeric ethylene–propylene–diene terpolymers [14].

2.4   POLYMERS FROM TERPENES

Abundant terpenes constitute the logical precursors to polyterpenic materials destined for bulk applications. In this context, pinenes, readily isolated on an industrial scale from turpentine, are obvious candidates. Although less abundant than α-pinene, β-pinene is by far the most studied homologue because of the higher reactivity of its exo-cyclic double bond in cationic polymerization. A considerable number of other monoterpenes have been tested as polymer precursors, using different polymerization mechanisms.

It is particularly relevant to this chapter and indeed to this book that the very first mention of the synthesis of a macromolecular material should have been through the use of a naturally occurring monomer mixture, namely turpentine. It was in fact Bishop Watson who reported in 1798 that the addition of a drop of sulphuric acid to turpentine produced a sticky resin, but it took another century for chemists to recognize that the properties of this material resembled those of natural rubber [15]. Another half century elapsed before the first systematic studies of the polymerization of terpenes, namely myrcene [16] and α- and β-pinene [17], were reported.

2.4.1 Conventional cationic polymerization

2.4.1.1 β-Pinene

The cationic polymerization of β-pinene (together with α-pinene) in toluene was first studied using several Lewis acid metal halides like AlCl₃, AlBr₃ and ZrCl₄, as initiators [17]. The high reactivity of the exomethylene double bond, the strain release resulting from the opening of the fused cyclobutane ring and the formation of a relatively stable tertiary carbenium ion are the driving forces of this reaction. The proposed polymerization mechanism (Fig. 2.6) involves the formation of a strong proton donor by the reaction of the Lewis acid with adventitious water (cocatalysis), followed by the protonation of the pinene molecule, whose ensuing carbenium ion rearranges to form a *p*-menthane type carbocation responsible for the propagation reaction [6, 17]. This process is extremely rapid and highly exothermic. In order to obtain polymers with viable molecular weights of a few thousand, the polymerization temperature must be particularly low, viz. around −40°C [6, 17], to reduce the relative kinetic contribution of the transfer reaction with respect to chain propagation (Fig. 2.6), a common feature in the cationic polymerization of aliphatic monomers.

Very recently, the cationic polymerization of β-pinene in toluene, using AlCl₃ as the initiator, was shown to proceed smoothly and rather rapidly under microwave irradiation [18].

Other Lewis acid initiators such as SnCl₄, TiCl₄, BF₃ and Et₂AlCl in various solvents and temperature ranges, were also studied [19], and polymers with Mn values in the range of 720–2 800 were obtained. In this study, it was shown that TiCl₄ and Et₂AlCl were the most efficient initiators, dichloromethane the best solvent and −80°C to 0°C the most suitable temperature range.

Of the numerous classical Lewis acids tested as initiators for the polymerization of β-pinene, EtAlCl₂ has proved by far the most efficient, particularly in terms of the possibility of preparing polymers with high molecular weights. Three studies have tackled this system over the last 15 years [20–22] using different strategies, particularly in the
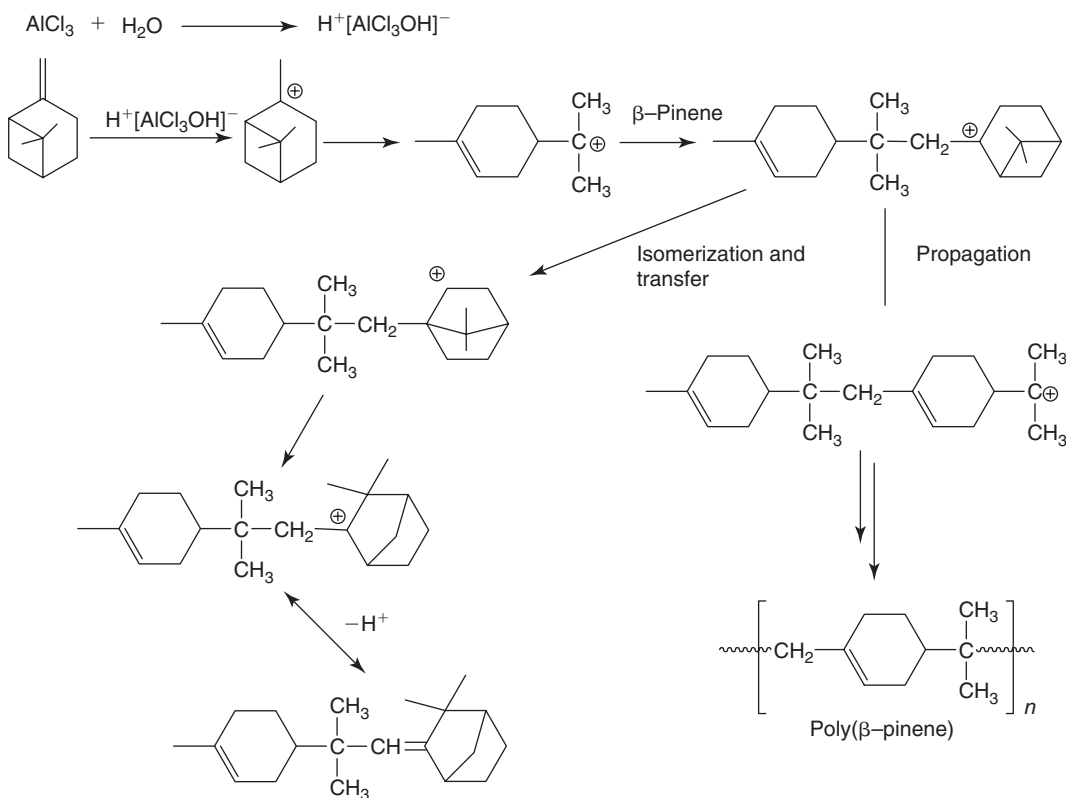
Figure 2.6   General mechanism of the cationic polymerization of β-pinene catalyzed by AlCl₃.

addition of specific bases, including 2,6-di-*tert*-butylpyridine, with its well-known property of proton trap, incapable of reacting with Lewis acids. The most interesting practical outcome of these investigations is associated with the attainment of Mn values which are particularly high for this monomer, ranging from 10 000 to 40 000, when working at low temperature [20, 22] and of a few thousand when working around room temperature [21]. These high-Mn poly(βPIN)s displayed a glass transition temperature of 90°C, which was further increased to 130°C after the polymer was hydrogenated [22].

Finally, the radiation-induced polymerization of β-pinene has also been studied [23]. Under extremely dry conditions, molecular weights in the range of 1 700–2 400 were obtained through a mechanism which was adequately demonstrated as being cationic in nature.

2.4.1.2   α-Pinene

Although α-pinene is readily protonated to form a tertiary carbocation, which can then rearrange to an unsaturated *p*-menthane isomer (Fig. 2.7), the attack of the endocyclic double bond to the isopropenyl cationic site is limited by steric hindrance.

The first reported study of the cationic polymerization of α-pinene [17] showed indeed that this isomer was vastly less reactive than its β-homologue because of the steric crowding associated with the polymerizable unsaturation. Experiments carried out at low temperature using various Lewis acid initiators gave extremely poor yields that were maximized only by working at 40°C, with the inevitable drawback of the drastic decrease in the molecular weight of the product, in fact mainly composed of dimeric structures [17]. An alternative α-pinene polymerization pathway involves the rearrangement of the tertiary pinane carbocation to a saturated secondary bornane isomer (Fig. 2.7). Both bornane and *p*-menthane repeating units (Fig. 2.7) have been detected in α-pinene homo- and co-polymers.

Despite this structural drawback, the fact that α-pinene is the most abundant turpentine component has spurred a considerable amount of research related to its cationic polymerization. Several laboratories have looked into the use of an initiating combination involving conventional Lewis acids and SbCl$_3$ as an activator [6, 24–28].

When the binary system AlCl$_3$/SbCl$_3$ was used in toluene at −15°C, poly(α-pinene)s with Mn of 1 140–1 600 were obtained [26, 27], with negligible proportions of dimers, as opposed to their high contribution in products prepared with only AlCl$_3$. Interestingly, whereas SbCl$_3$ seems essential for the optimization of α-pinene polymerization, its role in β-pinene polymerization is rather detrimental in terms of reaction rate and molecular weight distribution [27].

α-Pinene can also be polymerized using other aluminium halides (AlBr$_3$, AlEtCl$_2$) or other metal halides (BF$_3 \cdot$ OEt$_2$, SnCl$_4$, TiCl$_4$, WCl$_6$) in conjunction with SbCl$_3$ [24]. All these aluminium halides tend to produce lower poly(αPIN) yields and Mn values (typically about 80 per cent and 700, respectively) when compared to AlCl$_3$. The other metal halides were shown to yield high amounts of dimers (20–40 per cent) along with small amounts of oligomers [24]. The ^{1}H-NMR characterization of the polymers obtained with aluminium-based initiators showed that the unsaturated *p*-menthane moiety is the predominant repeating unit (81–95 per cent) with much smaller contributions from saturated bornane counterparts [24].

The addition of nucleophilic additives, such as esters (ethyl benzoate or ethyl acetate), ethers (ethyl ether and 1,4-dioxane) and ammonium salts (*n*Bu$_4$NCl) to the binary polymerization system AlCl$_3$/SbCl$_3$ allowed the α-pinene
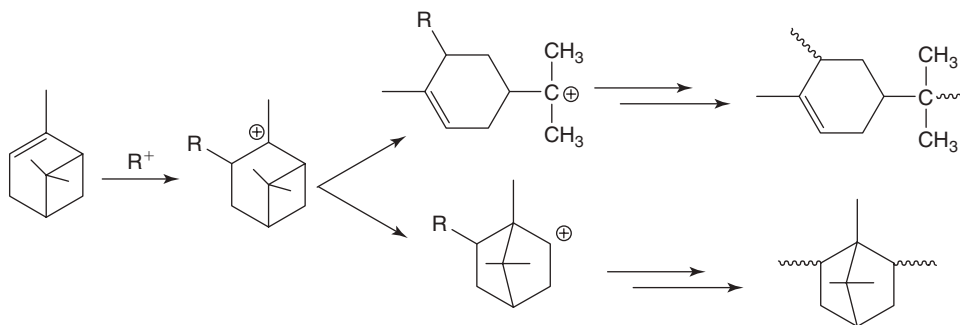
Figure 2.7   Alternative mechanisms of α-pinene cationic polymerization.

polymerization to be carried out at higher temperatures (0°C) without any significant decrease in molecular weights (Mn ~ 1 000) and with yields greater than 80 per cent with modest dimer contents (less than 6 per cent). However, these additives decreased the corresponding polymerization rates [25].

It has been reported that the cationic polymerization of α-pinene can be improved if, instead of using their simple mixture, SbCl$_3$ and AlCl$_3$ are previously melted together, thus favouring cross ionization by chloride ion transfer to give SbCl$_4^+$ as the direct initiating species, with Al$_2$Cl$_7^-$ as counter ion [29].

A recent addition to this topic deals with the hydrothermal deposit of AlCl$_3$ onto a zirconium mesoporous material and the use of the ensuing solid Lewis acid as a catalyst for both α-pinene polymerization and other conversions at room temperature [30].

### 2.4.1.3 Other terpenes and derivative

Several other terpenic components have been submitted to cationic polymerization. These include terpene oxides [31] and phellandrene [22]. The cationic polymerization of α- and β-pinene oxides, using BF$_3$ or PF$_5$ as initiators proceeded through the initial protonation of the oxyrane oxygen atom followed by the isomerization of the oxonium ion to give the tertiary exo-carbenium ion responsible for the chain growth, as shown in Fig. 2.8 [31]. This mechanism was corroborated by the ^{13}C-NMR of the ensuing polymers. However, this system was strongly affected by side reactions resulting from multiple rearrangements of the oxonium ion, which yielded a wide variety of secondary products and limited the polymer DP to 6–7 units [31].

The cationic polymerization of α-phellandrene, using EtAlCl$_2$, SnCl$_4$ or BF$_3$OEt$_2$ as initiators in various solvents produced polymers with Mn of 3 700–5 700 [22]. The cationic polymerization of limonene has also been reported [32] and its outcome found to be favoured by using the binary system AlCl$_3$/SbCl$_3$ instead of AlCl$_3$.

2.4.1.4 Copolymerization of β-pinene with synthetic monomers

The cationic random copolymerization of β-pinene with styrene and α-methylstyrene, initiated by AlCl$_3$ in dichloromethane, was investigated within a wide range of temperatures [33–35]. Regrettably, these studies were limited to a rather factual and empirical approach and left some major questions unanswered, such as the values of the reactivity ratios. The molecular weight of the copolymers, irrespective of the feed ratio and the reaction temperature, were very low in the first study [33] and increased somewhat in the subsequent ones [34, 35].

In the case of the β-pinene/isobutene combination initiated with EtAlCl$_2$, the ^{1}H-NMR spectrum of the copolymer showed an almost equal incorporation of the monomers and a high level of alternation [36].
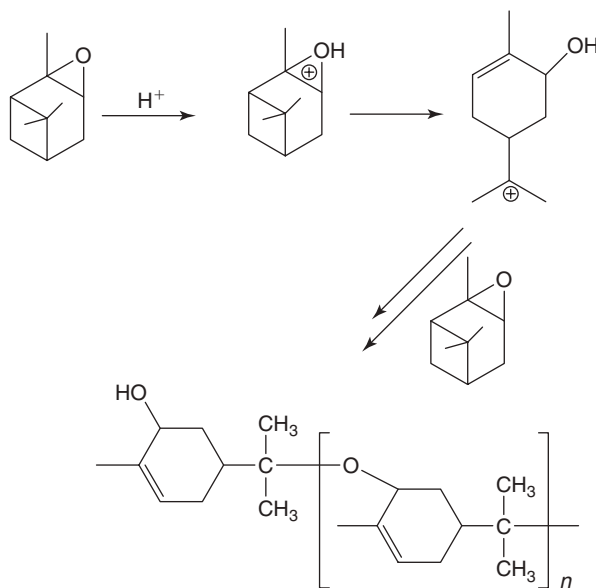
Figure 2.8   Cationic polymerization of α-pinene oxide.
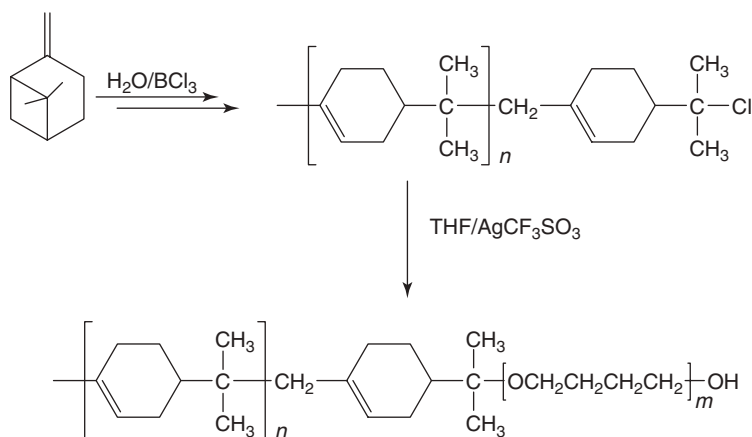
Figure 2.9 Synthesis of a di-block copolymers of β-pinene and THF through α-end chlorinated poly(βPIN).
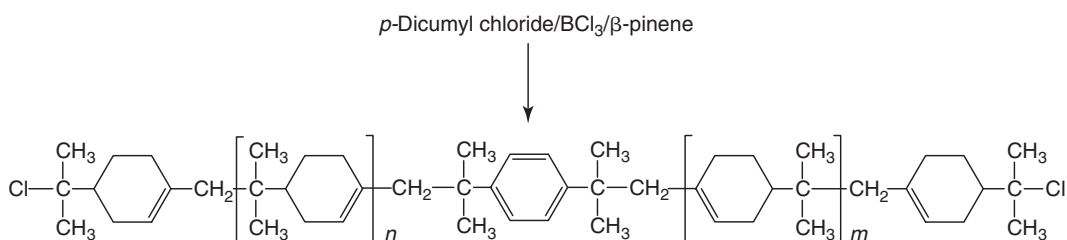
Figure 2.10 Synthesis of linear poly(βPIN) with two chlorine end groups.

The block copolymerization involving β-pinene has also been investigated [37]. This strategy involved the synthesis of a poly(βPIN) bearing tertiary chloride end groups and the attachment of poly(THF) blocks by their activation, as shown in Fig. 2.9 for chains with a single chlorinated site, thus giving a di-block structure.

When β-pinene was polymerized with BCl₃ in the presence of *p*-dicumylchloride or *p*-tricumylchloride, polymers with two (Fig. 2.10) and three (Fig. 2.11) chlorinated end groups were obtained as potential precursors for linear and star-shaped multi-block copolymers [37].

2.4.1.5 *Copolymerization of α-pinene with synthetic monomers*

The cationic copolymerization of α-pinene with several conventional monomers has been examined by various groups [38–41]. The reaction of α-pinene with isobutene using EtAlCl₂ in ethyl chloride at ∼ −100°C yielded random copolymers with Mn values in the range of 3 200–29 000, increasing with decreasing α-pinene feed [38]. The unsaturated *p*-menthane moiety was the dominant repeating unit in these copolymers [38]. The copolymerization of α-pinene and styrene using AlCl₃ as the initiator gave copolymers with Mn of 2 320–3 080 [39]. However, as in the case of α-pinene homopolymerization, the use of the SbCl₃/AlCl₃ combination here reduced the difference in monomer reactivity and produced higher copolymer yields [40, 41].

2.4.2 Living cationic polymerization

2.4.2.1 *Homopolymerization of β-pinene*

The cationic polymerization of β-pinene with conventional systems has been shown above to give modest and, exceptionally, medium molecular weights associated with rather broad distribution. The development of novel initiating systems capable of providing controlled cationic polymerizations in terms of *quasi*-living conditions (LCP)
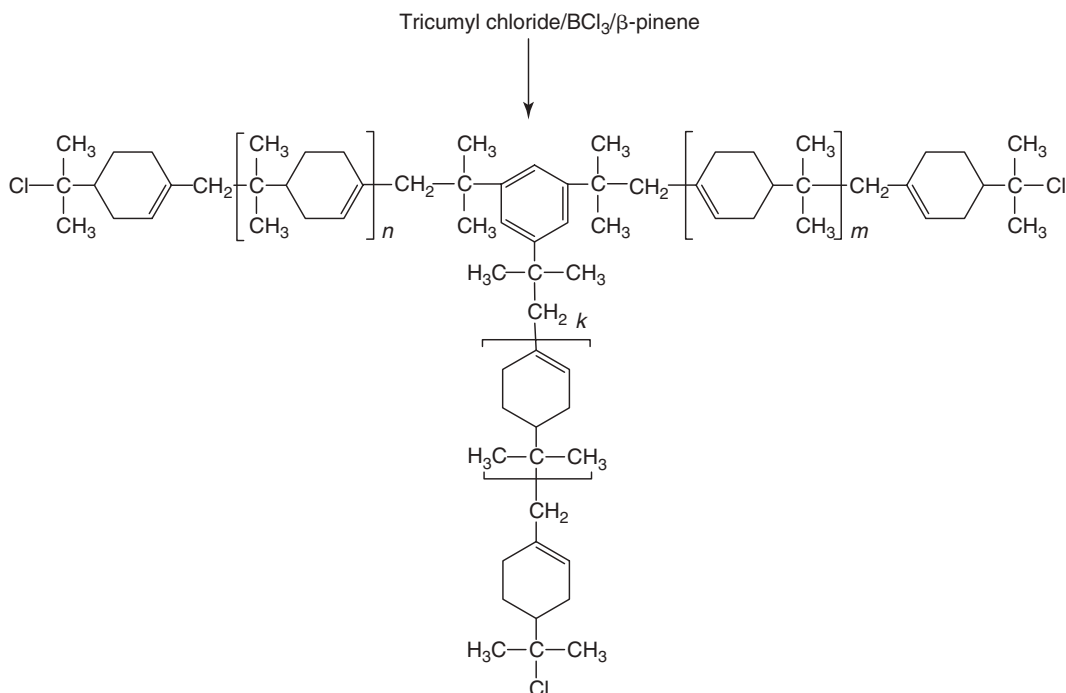
Figure 2.11   Synthesis of star-shaped poly(βPIN) with three chlorine end groups.

began some 20 years ago and was applied first to conventional monomers like styrene, isobutene and vinyl ethers, but this research was soon extended to terpenes after some failed attempts [20].

The first successful β-pinene LCP systems were reported by Lu *et al.* in 1997 [42–44]. The best conditions involved the use of the HCl adduct of 2-chloroethylvinyl ether, isopropoxytitanium chloride [Ti(O*i*Pr)Cl$_3$] in the presence of tetra-*n*-butylammonium chloride [*n*BuNCl] in dichloromethane at −40°C to −78°C, viz. a system previously optimized for the LCP of styrene [45]. The living character of this system was clearly demonstrated by the fact that Mn increased linearly with monomer conversion, even after several monomer additions [43].

The proposed polymerization mechanism [43, 44], shown in Fig. 2.12, involves the rearrangement of the pinane skeleton with the formation of a *p*-menthane type repeating unit, as unambiguously demonstrated from the ^{1}H-NMR spectrum of the ensuing polymer. It follows that the strain release resulting from the cyclobutane ring opening is still a key driving force in this propagation mechanism.

Other initiating systems were also shown to give LCP conditions, namely through the use of other Lewis acids [43] and coinitiators [43, 46].

2.4.2.2   *Copolymerization of β-pinene with synthetic monomers*

The synthesis of block, as well as random copolymers of β-pinene with styrene and *p*-methylstyrene (*p*MeSt), was studied by living cationic polymerization, using both the styrene and vinyl ether adducts as initiators in the presence of Ti(O*i*Pr)Cl$_3$ in methylene chloride at −40°C [44, 47]. For styrene (A) and β-pinene (B), both AB and BA block copolymers were obtained, as shown in Fig. 2.13, with Mn values of 4 000 and 3 600, respectively, and narrow Mw/Mn ratios (1.26 and 1.38, respectively). The efficiency of these block copolymerizations was attributed to the similar reactivity of the C—Cl bond derived from the two monomers [44].

The random living cationic polymerization of β-pinene with styrene and *p*MeSt was also inspected [44]. With the β-pinene/styrene mixtures, a faster consumption of the former monomer occurred, yielding tapered copolymers with Mn ~ 5 000 and MWD of 1.4 at 100/65 per cent consumption of β-pinene/styrene. In contrast, with the β-pinene/*p*MeSt mixtures, both monomers were consumed at nearly the same rate, yielding statistical copolymers with Mn ~ 5 000 and MWD of 1.5 at both monomer conversions higher than 90 per cent.
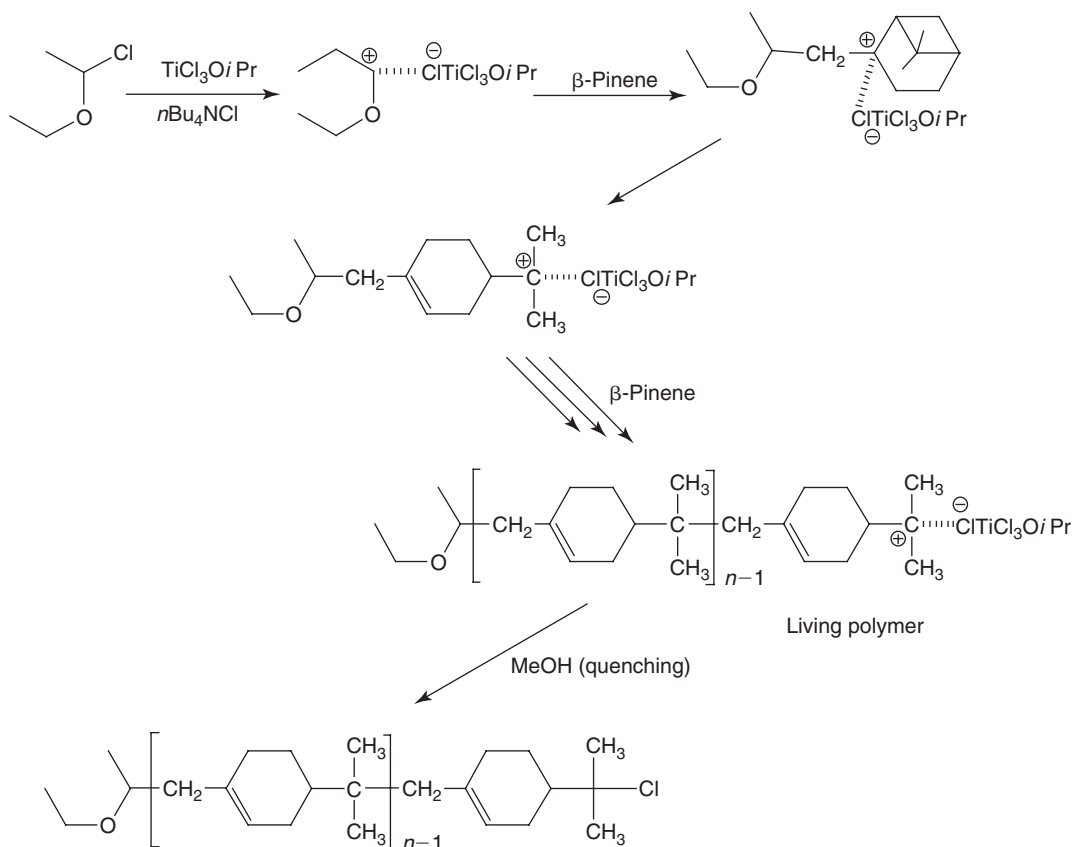
Figure 2.12   Mechanism of the LCP of β-pinene.
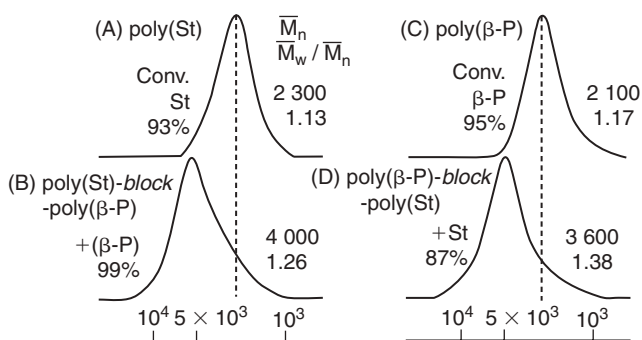
Figure 2.13   Molecular weight distribution curves for poly(St) A, poly(βPIN) B and the block copolymers obtained after addition of the other monomer (reprinted with permission from Reference [44]).

The random living cationic polymerization of β-pinene was also carried out with isobutene using 1-phenylethyl chloride/TiCl$_4$/Ti(OiPr)$_4$/nBu$_4$NCl [48]. Under these conditions, β-pinene and isobutene exhibited almost equal reactivities and were consumed at the same rate. This observation, together with proton NMR evidence, confirmed the random nature of the copolymer. Regardless of the monomer feed ratio, Mn increased with monomer conversion while preserving narrow MWDs (1.1–1.2), confirming the living character of the system [48].

Figure 2.14   Synthesis of methacrylic end-functionalized poly(βPIN) and poly(*p*MeSt)-block-poly(βPIN) by LCP.

In a different vein, the LCP synthesis of poly(βPIN) bearing benzyl chloride end groups [49, 50] opened the way to the insertion of a poly(THF) block by the activation of this moiety with $AgClO_4$ or $AgSbF_6$. The ensuing copolymer was thus made up of a non-polar rigid segment of poly(βPIN) linked to a polar, soft and semi-crystalline poly(THF) segment [49].

Grafted copolymers have also been prepared from the brominated poly(βPIN), whose synthesis is shown in Fig. 2.15, by the activation of the C—Br bonds with Et_2AlCl leading to the cationic sites for the polymerization of styrene [51].

2.4.3   Living cationic-radical copolymerization of β-pinene with synthetic monomers

The possibility of controlling the cationic polymerizations of β-pinene using the systems described above, opened an additional avenue of macromolecular engineering which consists in introducing reactive functional groups at one or both ends of poly(βPIN) or its copolymers and even within their backbone. The interest of these moieties is in their possible exploitation as starting sites for the free radical polymerization of a suitable monomer [42, 49, 50, 52].

Figure 2.14 illustrates this strategy applied to the specific context in which the terminal reactive moiety for both homo- and co-polymers of β-pinene prepared by LCP is a methacrylic group [42], from which the free radical polymerization of methyl methacrylate (MMA) was carried out to give block copolymers with interesting properties [42].

Figure 2.15 shows a different and more sophisticated approach to the combination of cationic and radical mechanisms, since in this case both processes bear a living character. Allylic brominated poly(βPIN) with Br/β-pinene unit ratios of 1.0 and 0.5 (Mn of 2 810 and 2 420, respectively and a similar MWD of 1.3) were obtained by treatment with *N*-bromosuccinimide/AIBN and then used as macroinitiators in conjunction with CuBr and 2,2′-bipyridine for the atom transfer radical polymerization (ATRP) of acrylic monomers [52, 53].

These grafting processes clearly require further optimization since some side reactions were reported to provoke the formation of insoluble gels [52].

2.4.4   Radical polymerization of monoterpenes

Although it is generally assumed that monoterpenes do not undergo radical homopolymerization, in some experiments dealing with the thermal treatment of β-pinene [54], it was shown that the material obtained must have been

Figure 2.15   Synthesis of poly(βPIN)-*g*-poly(MMA).

produced by a free radical mechanism, since cationic and anionic inhibitors did not affect this process [55]. More recently, the radical homopolymerizations of α- and β-pinene have indeed been more clearly confirmed [39, 56]. However, these processes which called upon AIBN as initiator, only gave oligomers (Mn ∼ 900) in modest yields (∼30 per cent) [56]. It is, therefore, reasonable to conclude that the original assumption, although strictly speaking inaccurate, reflects the actual reality in the sense that there is no interest in using free radical initiation to prepare materials based on the homopolymerization of monoterpenes.

This unfavourable situation is however reversed when pinenes and other monoterpenes are used as comonomers in free radical copolymerizations with monomers bearing structures other than theirs. These systems are described below as a function of the specific terpene comonomer.

2.4.4.1   Copolymerizations using pinenes

A considerable amount of attention has been devoted to this topic in recent years, particularly in view of the advances related to controlled radical polymerization [56–60].

The conventional free radical copolymerization of β-pinene and MMA or St, initiated by AIBN, yielded copolymers with Mw of about 11 600 and 25 400, respectively and MWD of 1.5 and 1.7, respectively [56]. When 2,3,4,5,6-pentafluorostyrene (PFS) was used as comonomer, and benzoyl peroxide as the initiator, a PFS-rich copolymer incorporating isolated isomerized β-pinene units distributed between poly(PFS) segments was obtained [57]. This feature is related to the low reactivity of the β-pinene free radicalar towards its monomer, that is to a reactivity ratio close to zero. These PFS-β-pinene copolymers were shown to combine the typical high water contact angles of perflourinated polymers (hydrophobicity) with the optical activity of poly(βPIN) [57]. A recently published study indicated that the radical random copolymerization of both α- and β-pinene with styrene under microwave irradiation yields materials with Mn values considerably higher than those obtained under conventional conditions, but still with very low conversions [18].

The radical copolymerization of β-pinene with acrylonitrile (AN) using AIBN as the initiator produced very low product yields with Mn ∼ 7 200 and MWD of 1.6 [59]. Again, the reactivity ratio relative to the terpenic monomer was close to zero and that of AN was 0.66, which produced a structure (Fig. 2.16) similar to that described above for PFS. This study had the added quality of kinetics and ^{1}H-NMR structural insights [59]. The addition of Lewis acids (TiCl$_4$, SnCl$_4$, ZnCl$_2$ and Et$_n$AlCl$_{3-n}$) produced an enhanced tendency to alternation, through the reduction of the reactivity ratio of AN to about 0.11, which resulted in an increase in the incorporation of β-pinene to levels as high as 43 per cent, that is to the formation of nearly alternated copolymer structures. Moreover, in the specific instance of EtAlCl$_2$ and especially of Et$_2$AlCl, higher copolymer yields were also obtained [59].
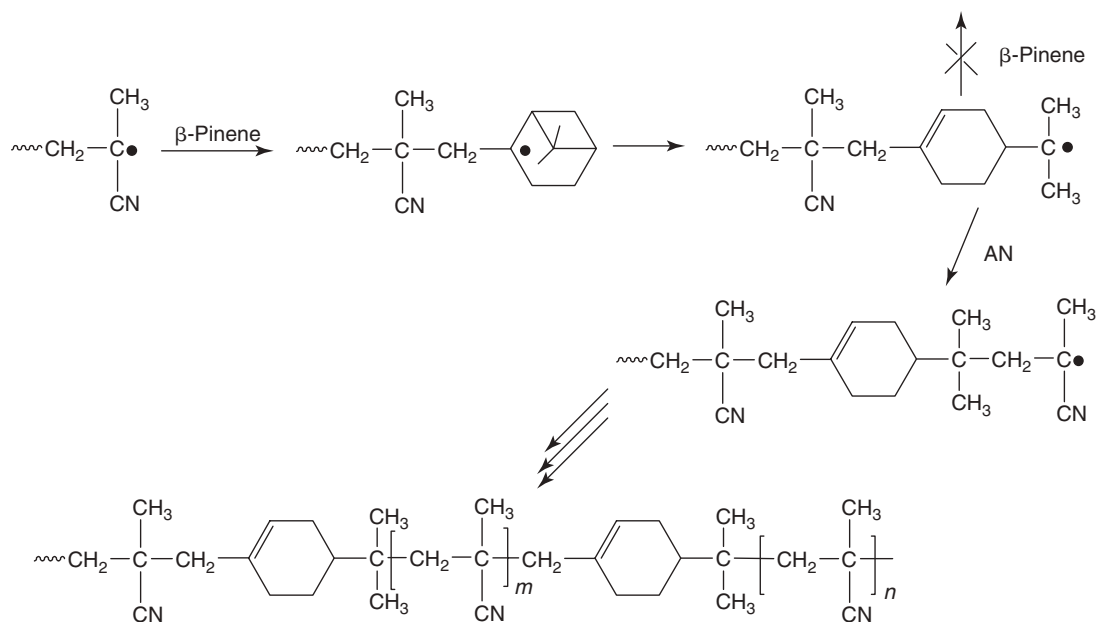
Figure 2.16   Proposed mechanism for the radical copolymerization of β-pinene and AN.

In the same study, the authors also investigated the use of the reversible addition-fragmentation transfer (RAFT) technique and showed that several such systems gave rise to a better controlled copolymerization, although the polydispersity of the ensuing copolymers depended on the nature of the actual agent used [59]. The most effective were cumyl dithiobenzoate (CDB) and 2-cyanopropyl-2-yl dithiobenzoate (CPDB) which gave polydispersities of 1.4 and 1.2, respectively. The living nature of these processes was confined to their first phase, since at high conversions the kinetics and Mn values strongly deviated from those predicted by a living system [59]. When Et$_2$AlCl was added to these optimized RAFT copolymerizations, both a narrow MWD (1.2) and a high β-pinene incorporation were achieved, suggesting a better reaction control and a higher tendency to alternation [59]. In spite of these improvements, the fact that the Mn of the copolymers did not increase with conversion, showed that even this system did not display a living character [59].

The AIBN-initiated radical copolymerization of β-pinene and methyl acrylate (MA) [58] with *n*-butyl acrylate (*n*BA) [60] produced results similar to those described above for AN [59] and thus the structure of the ensuing macromolecules were characterized by the presence of MA or *n*BA blocks alternated with single β-pinene units but the incorporation of β-pinene could again be enhanced by the addition of Et$_2$AlCl [58, 60]. When the authors attempted to turn this system into a controlled process by using RAFT reagents, the results were rather disappointing in the case of MA [58], whereas, when *n*BA was used [60], the results obtained were similar to those reported for AN [59].

To the best of our knowledge, only one publication describes the free radical copolymerization of α-pinene [56]. In this study, both MMA and St were studied as comonomers under standard conditions. Interestingly, it was shown that α-pinene is a more suitable comonomer than its β-isomer, since it gave higher rates, conversions and molecular weights under the same conditions [56]. Surprisingly, despite these more favourable features, α-pinene has not been investigated further in this context.

2.4.4.2   Copolymerization of limonene

The radical copolymerization of limonene with MMA [61, 62], AN [63], St [64] and *N*-vinylpirrolidone [65] gave alternating copolymers because both reactivity ratios were close to zero. Figure 2.17 shows the mechanism proposed for this process in the case of MMA.

More recently, liquid crystalline materials based on modified limonene–MMA copolymers have been described [66].

Finally, copolymers of limonene and maleic anhydride [67, 68] and terpolymers combining limonene with either MA and AN [69], or with St and MMA [70], have also been reported.

Initiation

Propagation

Monomer transfer
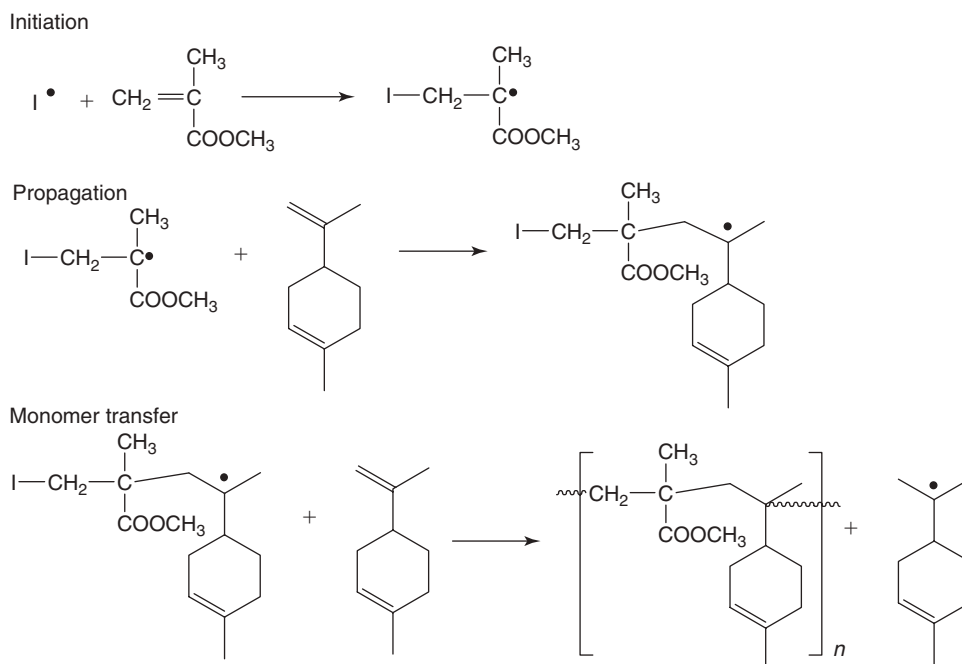
Figure 2.17 Proposed mechanism for the radical copolymerization of limonene and MMA.

2.4.4.3 *Copolymerization of monoterpene alcohols*

Like their hydrocarbon counterparts, most monoterpene alcohols do not undergo radical homopolymerization, but intervene in copolymerization with conventional monomers. The interest of the ensuing copolymers resides essentially in the fact that they bear a pendant hydroxyl group *per* terpene monomer unit.

α-Terpineol readily copolymerizes with MMA [71], St [72] and BMA [73]. In all these systems, the reactivity ratios were found to be very low, which favoured a high degree of alternation in the ensuing materials [71–73]. Fig. 2.18 depicts the mechanism proposed for the system involving MMA as comonomer [72].

Other authors have proposed mechanisms which differ from the one shown in Fig. 2.18, particularly in terms of the structure of the terpinyl free radical and hence of the structure of the corresponding monomer unit in the copolymers [71, 72, 74].

More recently, the radical copolymerization of α-terpineol with *N*-vinylpirrolidone was also studied. In this instance, the comonomers showed substantially different reactivity ratios resulting in the formation of random copolymers [75].
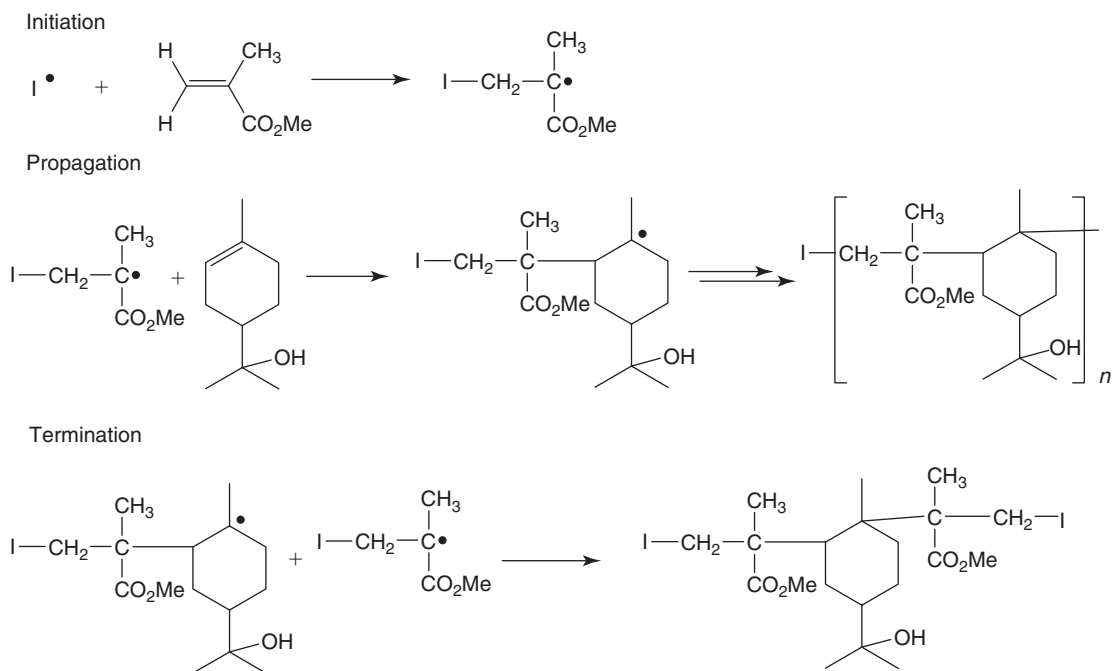
The radical copolymerization of linalol with AN [76], acrylamide [77], St [78] and BMA [79] yielded strongly alternating copolymers because of the very low reactivity ratios of both monomers (Fig. 2.19). The proposed polymer structures, as shown in Fig. 2.19 for the copolymer with AN, also involve the formation of the more stable tertiary radical intermediate [76, 77].

Likewise, the radical copolymerization of citronellol with vinyl acetate [80], St [81] and acrylamide [82] produced alternating copolymers whose structures evoke the same radical mechanism.

On the other hand, geraniol showed a substantially different reactivity in its copolymerization with St, leading to a lower alternating character [83].

Finally, it is worth mentioning that several radical terpolymerization studies using linalol [84, 85] and citronellol [86] have been carried out.

The obvious interest in interpenetrating polymer networks (IPN) based on very different macromolecular structures has spurred some studies involving terpenols. Thus the synthesis of IPN involving poly(St) and poly(citronellol-*alt*-MMA) [87] and of poly(α-terpineol-co-St) with ethyl acrylate crosslinked with divinylbenzene have been reported [74].

Initiation

Propagation

Termination

Figure 2.18   Proposed mechanism for the radical copolymerization of α-terpineol with MMA.
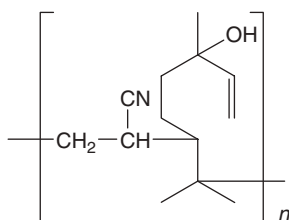
Figure 2.19   Structure of the linalol/AN copolymer.

An interesting exploitation of the OH side groups borne by these copolymers is provided by a recent study in which poly(α-terpineol-co-MMA) was modified by grafting phenyl benzoate mesogenic groups, bearing vinyl terminated polymethylene spacers, to give liquid crystalline materials [88].

2.4.5 Other monomers and polymerization systems

The emulsion polymerization of myrcene and its copolymerization with styrene and butadiene, followed by vulcanization of the ensuing polymers to obtain synthetic rubbers was reported as early as 1948 [16] but no other such system has been mentioned in the literature since then.

Only a few studies have been devoted to the Ziegler–Natta polymerization of terpene monomers. α- and β-pinene, limonene and camphene were investigated by various authors and the corresponding homopolymers were shown to be structurally analogous to those obtained by cationic mechanisms [89, 90]. More recently, this type of catalysis was successfully applied to copolymerization systems involving α-pinene and MMA or St [56].

Myrcene is, to our knowledge, the only monoterpene which has been the object of living anionic polymerization (LAP) and copolymerization studies [91]. These systems involved *N*-butyl lithium as the initiator, and either benzene or THF as solvent. When the reaction was carried out in the former, 1,4-addition was favoured (85–90 per cent),
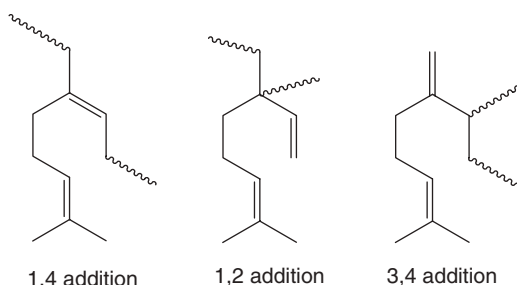
Figure 2.20   Structure of the 1,4- 1,2- and 3,4-type myrcene monomer units.

followed by 3,4-addition (11–15 per cent), whereas in THF, 1,4-addition accounted for only 39–44 per cent, followed by 3,4-addition, with 39–44 per cent, and by 1,2-addition, with 10–18 per cent (Fig. 2.20).

The corresponding copolymerization with styrene in benzene yielded a polymer rich in myrcene with a poly(St) block formed in the later polymerization stages. In THF, a styrene-rich copolymer was obtained in the early stages, with a polymyrcene block formed towards the end [91].

Alternating copolymers of limonene oxide and carbon dioxide have been prepared using β-diiminate zinc acetate complexes [92]. These polycarbonate-type copolymers had rather low Mn values (5 500–11 000), but narrow MDWs (close to 1.1). Cataldo and Keheyan [93] studied recently the polymerization of (—)-β-pinene with ψ-radiation, and found that the product was optically active, although such a feature had not been mentioned in earlier studies by other authors [94, 95].

2.5   POLYTERPENE APPLICATIONS

2.5.1   Tack and adhesion

Commercially available polyterpene resins, and particularly poly(PIN)s, are low molecular weight hydrocarbon-like polymers used as adhesive components to impart tack (to both solvent-based and hot-melt systems), provide high gloss, good moisture vapour transmission resistance and good flexibility for wax coating and ensure viscosity control and density increase to casting waxes. There is a considerable similarity in the context of these properties between rosin derivatives (see corresponding chapter in this book) and polyterpenes.

The ageing stability of an adhesive depends, to some extent, on the corresponding stability of its tackifing resin [96, 97]. Since poly(PIN)s contain unsaturations in their chemical structures, they are sensitive to atmospheric oxidation, which leads to the progressive loss of their tack. Photo-oxidation studies have shown that both poly(PIN)s behave similarly in this context, with α,β-unsaturated hydroperoxides as the primary products, which then undergo photolysis to give various low molecular weight degradation fragments [96]. Under thermal oxidation conditions, similar ageing processes are observed, but the reactivity of the two poly(PIN)s is now significantly different with the α-homologue being more fragile [97].

2.5.2   Other applications of polyterpenes and terpenes

Poly(βPIN) was used as a spray adjuvant in pesticide applications to crops to increase their deposition and to decrease their rate of decay, which resulted in increased efficiency [98]. This effect is achieved through the formation of an organic film covering the crop foliage, which protects the active component from rain and wind erosion as well as volatilization.

It was recently shown that doping poly(βPIN) with iodine produces a semi-conductive material, with conductivities of about 8×10^{-3} S cm^{-1}, typical of non-conjugated doped polymers [99]. This material also showed a large quadratic electro-optic effect which would make it useful for non-linear optics applications [100].

In recent years, some monoterpenes have attracted some interest as environment-friendly solvents for polymeric systems. Camphene, which is both harmless and readily sublimed, has been tested as solvent for polypropylene

[101, 102]. The thermally induced phase separation of these solutions was applied to the preparation of microporous polypropylene tubular membranes [102, 103]. Camphene has also been used in the preparation of gas-filled polymeric micro-bubbles by freeze drying polymer/camphene emulsions [104–106]. These spheres can be used as contrast agents for the medical ultrasonography of vital organs.

It has been shown that α-pinene oxide, in conjunction with $ZnEt_2$, constitutes an efficient catalytic system for the stereospecific polymerization of styrene oxide [107].

Limonene was tested as a solvent for recycling polystyrene [108], as well as a renewable polymerization solvent and chain transfer agent in ring-opening metathesis polymerizations [109].

Finally, poly(α-PIN) was used in the nonisothermal crystallization of isotactic polypropylene from blends containing up to 30 per cent of this polyterpene [110–112].

2.6   CONCLUDING REMARKS

Although the following observations might sound redundant in their similarity to the conclusions of many, if not all the chapters of this book, they reflect nonetheless what we consider as being very relevant points. The systematic literature survey that we carried out to ensure the comprehensive coverage of this chapter showed unambiguously that the last decade has witnessed a drastic increase in scientific and more applied research related to terpenes as source of materials. It seems obvious to us that the concept and the practical implementation of a biorefinery, that is the rational exploitation of renewable resources, find in terpenes an excellent additional justification.

REFERENCES

1. Erman W.F., *Chemistry of Monoterpenes*, Marcel Dekker, New York, 1985.
2. Ruzicka L., The isoprene rule and the biogenesis of terpenic compounds, *Experientia*, **9**(10), 1953, 357–367.
3. Albert R.M., Webb R.L., in *Fragrance and Flavour Chemicals* (Eds. Zinkel D.F. and Russel J.), Pulp Chemical Association, New York, 1989, pp. 479–509.
4. Breitmaier E., *Terpenes: Flavors, Fragrances, Pharmaca, Pheromones*, Wiley-VCH, Weinheim, 2006.
5. Buntin G.A., in *Insecticides* (Eds. Zinkel D.F. and Russel J.), Pulp Chemical Association, New York, 1989, pp. 531–559.
6. Ruckel E.R., Arlt H.J., in *Polyterpene Resins* (Eds. Zinkel D.F. and Russel J.), Pulp Chemical Association, New York, 1989, pp. 510–530.
7. Kelly M.J., Rohl A.E., in *Pine Oil and Miscellaneous Uses* (Eds. Zinkel D.F. and Russel J.), Pulp Chemical Association, New York, 1989, pp. 560–573.
8. Zinkel D.E., Russel J., *Naval Stores. Production, Chemistry, Utilization*, Pulp Chemical Association, New York, 1989.
9. Stauffer D.F., in *Production, Markets and Economics* (Eds. Zinkel D.F. and Russel J.), Pulp Chemical Association, New York, 1989, pp. 39–82.
10. Coppen J.J.W., Hone G.A., *Gum Naval Stores: Turpentine and Rosin from Pine Resin*, FAO, Rome, 1995.
11. Stauffer D.F., Production, markets and economics, in *Naval Stores. Production, Chemistry, Utilization* (Eds. Zinkel D.F. and Russel J.), Pulp Chemical Association, New York, 1989, pp. 39–82.
12. Derfer J.M., Traynor S.G., in *Chemistry of Turpentine* (Eds. Zinkel D.F. and Russel J.), Pulp Chemical Association, New York, 1989, pp. 225–260.
13. Cascaval C.N., Ciobanu C., Rosu L., Rosu D., Turpentine as the raw chemicals for the polymerization processes, *Mater. Plast.*, **42**(3), 2005, 229–232.
14. Dolatkhani M., Cramail H., Deffieux A., Linear nonconjugated dienes from biomass as termonomers in EPDM synthesis, 1. Study of their reactivity in homopolymerizations, copolymerizations and terpolymerizations, *Macromol. Chem. Phys.*, **196**(10), 1995, 3091–3105.
15. Ruckel E.R., Wojcik R.T., Arlt H.G., Cationic polymerization of alpha-pinene oxide and beta-pinene oxide by a unique oxonium ion-carbenium ion sequence, *Abstracts of Papers of the American Chemical Society*, **173**(MAR20), 1977, 49.
16. Johanson A.J., McKennon F.L., Goldblatt L.A., Emulsion polymerization of myrcene, *Ind. Eng. Chem.*, **40**(3), 1948, 500–501.
17. Roberts W.J., Day A.R., A study of the polymerization of alpha-pinene and beta-pinene with Friedel Crafts type catalysts, *J. Am. Chem. Soc.*, **72**(3), 1950, 1226–1230.
18. Barros M.T., Petrova K.T., Ramos A.M., Potentially biodegradable polymers based on alpha- or beta-pinene and sugar derivatives or styrene, obtained under normal conditions and on microwave irradiation, *Eur. J. Org. Chem.*(8), 2007, 1357–1363.

19. Martinez F., Cationic polymerization of beta-pinene, *J. Polym. Sci. A: Polym. Chem.*, **22**(3), 1984, 673–677.

20. Keszler B., Kennedy J.P., Synthesis of high-molecular-weight poly (beta-pinene), *Adv. Polym. Sci.*, **100**, 1992, 1–9.

21. Guine R.P.F., Castro J., Polymerization of beta-pinene with ethylaluminum dichloride ($C_2H_5AlCl_2$), *J. Appl. Polym. Sci.*, **82**(10), 2001, 2558–2565.

22. Satoh K., Sugiyama H., Kamigaito M., Biomass-derived heat-resistant alicyclic hydrocarbon polymers: poly(terpenes) and their hydrogenated derivatives, *Green Chem.*, **8**(10), 2006, 878–882.

23. Adur A.M., Williams F., Radiation-induced cationic polymerization of beta-pinene, *J. Polym. Sci. A: Polym. Chem.*, **19**(3), 1981, 669–678.

24. Higashimura T., Lu J., Kamigaito M., Sawamoto M., Deng Y.X., Cationic polymerization of alpha-pinene with aluminum-based binary catalysts. 2, *Makromol. Chem.-Macromol. Chem. Phys.*, **194**(12), 1993, 3441–3453.

25. Higashimura T., Lu J., Kamigaito M., Sawamoto M., Deng Y.X., Cationic polymerization of alpha-pinene with aluminum-based binary catalysts. 3. Effects of added base, *Makromol. Chem.-Macromol. Chem. Phys.*, **194**(12), 1993, 3455–3465.

26. Higashimura T., Lu J., Kamigaito M., Sawamoto M., Deng Y.X., Cationic polymerization of alpha-pinene with the binary catalyst Alcl3/Sbcl3, *Makromol. Chem.-Macromol. Chem. Phys.*, **193**(9), 1992, 2311–2321.

27. Lu J., Kamigaito M., Sawamoto M., Higashimura T., Deng Y.X., Cationic polymerization of beta-pinene with the AlC3/SbCl3 binary catalyst: Comparison with alpha-pinene polymerization, *J. Appl. Polym. Sci.*, **61**(6), 1996, 1011–1016.

28. Radbil A.B., Zhurinova T.A., Starostina E.B., Radbil B.A., Preparation of high-melting polyterpene resins from alpha-pinene, *Russ. J. Appl. Chem.*, **78**(7), 2005, 1126–1130.

29. Lu J., Liang H., Zhang R.J., Deng Y.X., Cationic polymerization of alpha-pinene initiated by AlCl3/SbCl3 – Studies on the nature of the initiating species, *Chem. J. Chin. Univ.*, **17**(8), 1996, 1314–1318.

30. Li L., Yu S.T., Liu F.S., Yang J.Z., Zhaug S.F., Reactions of turpentine using Zr-MCM-41 family mesoporous molecular sieves, *Catal. Lett.*, **100**(3–4), 2005, 227–233.

31. Ruckel E.R., Wojcik R.T., Arlt H.G., Cationic polymerization of alpha-pinene oxide and beta-pinene oxide by a unique oxonium ion carbenium ion sequence, *J. Macromol. Sci. Chem.*, **A10**(7), 1976, 1371–1390.

32. Lu J., Liang H., Zhang R.J., Deng Y.X., Comparison of cationic polymerization of alpha- and beta-pinenes and limonene, *Acta Polym. Sinica*(6), 1998, 698–703.

33. Pietila H., Sivola A., Sheffer H., Cationic polymerization of beta-pinene, styrene and alpha-methylstyrene, *J. Polym. Sci. A1 Polym. Chem.*, **8**(3), 1970, 727–737.

34. Snyder C., McIver W., Sheffer H., Cationic polymerization of beta-pinene and styrene, *J. Appl. Polym. Sci.*, **21**(1), 1977, 131–139.

35. Sheffer H., Greco G., Paik G., The characterization of styrene beta-pinene polymers, *J. Appl. Polym. Sci.*, **28**(5), 1983, 1701–1705.

36. Kennedy J.P., Chou T., Sequence distribution analysis of isobutylene–styrene and isobutylene–isoprene copolymers, *J. Macromol. Sci. Chem.*, **A10**(7), 1976, 1357–1369.

37. Kennedy J.P., Liao T.P., Guhaniyogi S., Chang V.S.C., New telechelic polymers and sequential copolymers by poly-functional initiator-transfer agents (infers). 19. Poly(beta-pinenes) carrying one, two, or three functional end groups. 1. The effect of reaction conditions on the polymerization of beta-pinene, *J. Polym. Sci. A: Polym. Chem.*, **20**(11), 1982, 3219–3227.

38. Kennedy J.P., Nakao M., Co-polymerization of isobutylene with alpha-pinene, *J. Macromol. Sci. Chem.*, **A11**(9), 1977, 1621–1636.

39. Khan A.R., Yousufzai A.H.K., Jeelani H.A., Akhter T., Copolymers from alpha-pinene. 2. Cationic copolymerization of styrene and alpha-pinene, *J. Macromol. Sci. Chem.*, **A22**(12), 1985, 1673–1678.

40. Deng Y.X., Peng C.P., Duan W., Zhang R.J., Zeng L.M., Studies on the cationic copolymerization of alpha-pinene and styrene with the AlCl3/SbCl3 catalyst, *Chem. J. Chin. Univ.*, **17**(9), 1996, 1467–1472.

41. Deng Y.X., Peng C.P., Liu P., Lu J., Zeng L.M., Wang L.C., Studies on the cationic copolymerization of alpha-pinene and styrene with complex SbCl3/AlCl3 catalyst systems. 1. Effects of the polymerization conditions on the copolymerization products, *J. Macromol. Sci.: Pure Appl. Chem.*, **A33**(8), 1996, 995–1004.

42. Lu J., Kamigaito M., Sawamoto M., Higashimura T., Deng Y.X., Living cationic isomerization polymerization of beta-pinene. 3. Synthesis of end-functionalized polymers and graft copolymers, *J. Polym. Sci. A: Polym. Chem.*, **35**(8), 1997, 1423–1430.

43. Lu J., Kamigaito M., Sawamoto M., Higashimura T., Deng Y.X., Living cationic isomerization polymerization of beta-pinene. Initiation with HCl-2-chloroethyl vinyl ether adduct TiCl3(OiPr) in conjunction with nBu(4)NCl, *Macromolecules*, **30**(1), 1997, 22–26.

44. Lu J., Kamigaito M., Sawamoto M., Higashimura T., Deng Y.X., Living cationic isomerization polymerization of beta-pinene. 2. Synthesis of block and random copolymers with styrene or *p*-methylstyrene, *Macromolecules*, **30**(1), 1997, 27–31.

45. Hasebe T., Kamigaito M., Sawamoto M., Living cationic polymerization of styrene with TiCl3(OiPr) as a Lewis acid activator, *Macromolecules*, **29**(19), 1996, 6100–6103.

46. Lu J., Liang H., Zhang R.F., Living cationic polymerization of beta-pinene with 1-phenylethyl chloride/TiCl$_4$/Ti(OiPr)(4), *Chem. J. Chin. Univ.*, **21**(12), 2000, 1932–1935.
47. Lu J., Liang H., Li B.E., Synthesis of block and graft copolymers of beta-pinene, *Acta Polym. Sinica*(6), 2001, 755–759.
48. Li A.L., Zhang W., Liang H., Lu J., Living cationic random copolymerization of beta-pinene and isobutylene with 1-phenylethyl chloride/TiCl$_4$/Ti(OiPr)(4)/nBu(4)NCl, *Polymer*, **45**(19), 2004, 6533–6537.
49. Lu J., Liang H., Zhang R.F., Li B., Synthesis of poly(beta-pinene)-b-polytetrahydrofuran from beta-pinene-based macroinitiator, *Polymer*, **42**(10), 2001, 4549–4553.
50. Lu L., Liang H., Li B., Zhang W., Synthesis of benzyl chloride capped beta-pinene macroinitiator and block copolymers, *Acta Polym. Sinica*(3), 2001, 357–360.
51. Hui L., Jiang L., Synthesis of poly(beta-pinene)-*g*-polystyrene from allylic brominated poly(beta-pinene), *J. Appl. Polym. Sci.*, **75**(5), 2000, 599–603.
52. Lu J., Liang H., Zhang W., Cheng Q., Synthesis of poly(beta-pinene)-*g*-poly(meth)acrylate by the combination of living cationic polymerization and atom transfer radical polymerization, *J. Polym. Sci. A: Polym. Chem.*, **41**(9), 2003, 1237–1242.
53. Li A.L., Liang H., Lu J., Synthesis of copolymers of beta-pinene by the combination of living cationic polymerization and ATRP, *Acta Polym. Sinica*(1), 2006, 151–155.
54. Kennedy J.P., Chou T., Crystalline poly(beta-pinene), *J. Polym. Sci. C: Polym. Lett.*, **14**(3), 1976, 147–149.
55. Adur A.M., Williams F., Effects of inhibitors on the thermal polymerization of beta-pinene, *J. Polym. Sci. C: Polym. Lett.*, **19**(2), 1981, 53–57.
56. Ramos A.M., Lobo L.S., Polymers from pine gum components: Radical and coordination homo and copolymerization of pinenes, *Macromol. Symp.*, **127**, 1998, 43–50.
57. Paz-Pazos M., Pugh C., Synthesis of optically active copolymers of 2,3,4,5,6-pentafluorostyrene and beta-pinene with low surface energies, *J. Polym. Sci. A: Polym. Chem.*, **44**(9), 2006, 3114–3124.
58. Wang Y., Li A.L., Liang H., Lu J., Reversible addition-fragmentation chain transfer radical copolymerization of beta-pinene and methyl acrylate, *Eur. Polym. J.*, **42**(10), 2006, 2695–2702.
59. Li A.L., Wang Y., Liang H., Lu J., Controlled radical copolymerization of beta-pinene and acrylonitrile, *J. Polym. Sci. A: Polym. Chem.*, **44**(8), 2006, 2376–2387.
60. Li A.L., Wang X.Y., Liang H., Lu J., Controlled radical copolymerization of β-pinene and *n*-butyl acrylate, *React. Funct. Polym.*, **67**, 2007, 481–488.
61. Sharma S., Srivastava A.K., Alternating copolymers of limonene with methyl methacrylate: Kinetics and mechanism, *J. Macromol. Sci.: Pure Appl. Chem.*, **A40**(6), 2003, 593–603.
62. Sharma S., Srivastava A.K., Free radical copolymerization of limonene with butyl methacrylate: Synthesis and characterization, *Indian J. Chem. Technol.*, **12**(1), 2005, 62–67.
63. Sharma S., Srivastava A.K., Radical copolymerization of limonene with acrylonitrile: Kinetics and mechanism, *Polym.-Plast. Technol. Eng.*, **42**(3), 2003, 485–502.
64. Sharma S., Srivastava A.K., Synthesis and characterization of copolymers of limonene with styrene initiated by azobisisobutyronitrile, *Eur. Polym. J.*, **40**(9), 2004, 2235–2240.
65. Sharma S., Srivastava A.K., Radical co-polymerization of limonene with *N*-vinyl pyrrolidone: Synthesis and characterization, *Designed Monom. Polym.*, **9**(5), 2006, 503–516.
66. Mishra G., Srivastava A.K., Side-chain liquid-crystalline polymers with a limonene-co-methyl methacrylate main chain: Synthesis and characterization of polymers with phenyl benzoate mesogenic groups, *J. Appl. Polym. Sci.*, **102**(5), 2006, 4595–4600.
67. Maslinskasolich J., Kupka T., Kluczka M., Solich A., Optically-active polymers. 2. Copolymerization of limonene with maleic-anhydride, *Macromol. Chem. Phys.*, **195**(5), 1994, 1843–1850.
68. Doiuchi T., Yamaguchi H., Minoura Y., Cyclo-copolymerization of D-limonene with maleic-anhydride, *Eur. Polym. J.*, **17**(9), 1981, 961–968.
69. Shukla P., Ali A., Srivastava A.K., Optically active terpolymer: Synthesis and characterization, *J. Indian Chem. Soc.*, **77**(1), 2000, 48–49.
70. Sharma S., Srivastava A.K., Synthesis and characterization of a terpolymer of limonene, styrene, and methyl methacrylate via a free-radical route, *J. Appl. Polym. Sci.*, **91**(4), 2004, 2343–2347.
71. Yadav S., Srivastava A.K., Kinetics and mechanism of copolymerization of alpha-terpineol with methylmethacrylate in presence of azobisisobutyronitrile as an initiator, *J. Polym. Res. Taiwan*, **9**(4), 2002, 265–270.
72. Yadav S., Srivastava A.K., Copolymerization of alpha-terpineol with styrene: Synthesis and characterization, *J. Polym. Sci. A: Polym. Chem.*, **41**(11), 2003, 1700–1707.
73. Yadav S., Srivastava A.K., Synthesis of functional and alternating copolymer of alpha-terpineol with butylmethacrylate, *Polym.-Plast. Technol. Eng.*, **43**(4), 2004, 1229–1243.
74. Prajapati K., Varshney A., Terpene-based semi-interpenetrating polymer networks initiated by *p*-nitrobenzyl triphenyl phosphonium ylide: Synthesis and characterization, *Designed Monom. Polym.*, **9**(5), 2006, 453–476.

75. Yadav S., Srivastava A.K., Kinetics and monomer reactivity ratios of *N*-vinylpyrrolidone and alpha-terpineol, *J. Appl. Polym. Sci.*, **103**, 2007, 476–481.

76. Shukla A., Srivastava A.K., Kinetics and mechanism of copolymerization of linalool with acrylonitrile, *J. Macromol. Sci.: Pure Appl. Chem.*, **A40**(1), 2003, 61–80.

77. Shukla A., Srivastava A.K., Free radical copolymerization of acrylamide and linalool with functional group as a pendant, *High Perform. Polym.*, **15**(3), 2003, 243–257.

78. Shukla A., Srivastava A.K., Determination of reactivity ratios and kinetics of free radical copolymerization of linalool with styrene, *Polym. Adv. Technol.*, **15**(8), 2004, 445–452.

79. Pathak S., Srivastava A.K., Free radical co-polymerization of butylmethacrylate and linalool with a functional group as a pendant, *Designed Monom. Polym.*, **8**(5), 2005, 409–422.

80. Pandey P., Srivastava A.K., Benzoyl peroxide-initiated copolymerization of citronellol and vinyl acetate, *J. Polym. Sci. A: Polym. Chem.*, **40**(9), 2002, 1243–1252.

81. Srivastava A.K., Pandey P., Benzoyl peroxide-*p*-acetylbenzylidenetriphenyl arsoniumylide initiated copolymerization of citronellol and styrene, *Polym. Int.*, **50**(8), 2001, 937–945.

82. Srivastava A.K., Pandey P., Mishra G., Synthesis and characterization of functional copolymers of citronellol and acrylamide, *J. Appl. Polym. Sci.*, **102**(5), 2006, 4908–4914.

83. Srivastava A.K., Pandey P., Synthesis and characterisation of copolymers containing geraniol and styrene initiated by benzoyl peroxide, *Eur. Polym. J.*, **38**(8), 2002, 1709–1712.

84. Shukla A., Srivastava A.K., Terpolymerization of linalool, styrene, and methyl methacrylate: Synthesis, characterization, and a kinetic study, *Polym.-Plast. Technol. Eng.*, **41**(4), 2002, 777–793.

85. Srivastava A.K., Kamal M., Kaur M., Pandey S., Daniel N., Chaurasia A.K., Pandey P., Terpolymerization: A review, *J. Polym. Res. Taiwan*, **9**(3), 2002, 213–220.

86. Pandey P., Srivastava A.K., Synthesis and characterization of optically active and functional terpolymer of citronellol, styrene, and methyl methacrylate: A kinetic study, *Adv. Polym. Techol.*, **21**(1), 2002, 59–64.

87. Pandey P., Kamal M., Srivastava A.K., Interpenetrating polymer network of poly(styrene) and poly(citronellol-alt-methyl methacrylate). Synthesis and characterization, *Polym. J.*, **35**(2), 2003, 122–126.

88. Mishra G., Srivastava A.K., Side-chain liquid crystalline polymers with [alpha-terpineol-co-MMA] main chain: Synthesis and characterization of polymers with phenyl benzoate mesogenic group, *Polym. Bull.*, **58**(2), 2007, 351–358.

89. Marvel C.S., Hanley J.R., Longone D.T., Polymerization of beta-pinene with ziegler-type catalysts, *J. Polym. Sci.*, **40**(137), 1959, 551–555.

90. Modena M., Bates R.B., Marvel C.S., Some low molecular weight polymers of D-limonene and related terpenes obtained by Ziegler-type catalysts, *J. Polym. Sci. A: Gen. Papers*, **3**(3PA), 1965, 949–960.

91. Sivola A., *N*-butyllithium-initiated polymerization of myrcene and its copolymerization with styrene, *Acta Polytech. Scand.-Chem. Technol. Ser.*(134), 1977, 7–65.

92. Byrne C.M., Allen S.D., Lobkovsky E.B., Coates G.W., Alternating copolymerization of limonene oxide and carbon dioxide, *J. Am. Chem. Soc.*, **126**(37), 2004, 11404–11405.

93. Cataldo F., Keheyan Y., Radiopolymerization of beta(-)pinene: A case of chiral amplification, *Radiat. Phys. Chem.*, **75**(5), 2006, 572–582.

94. Bates T.H., Williams T.F., Radiolysis of terpene hydrocarbons – Isomerization and polymerization of alpha-pinene and beta-pinene, *Nature*, **187**(4738), 1960, 665–669.

95. Bates T.H., Best J.V.F., Williams T.F., Radiation chemistry of beta-pinene, *J. Chem. Soc.*(MAY), 1962, 1531–1540.

96. Binet M.L., Commereuc S., Chalchat J.C., Lacoste J., Oxidation of polyterpenes: A comparison of poly alpha, and poly beta, pinenes behaviours – Part I – Photo-oxidation, *J. Photochem. Photobiol. A: Chem.*, **120**(1), 1999, 45–53.

97. Binet M.L., Commereuc S., Verney V., Thermo-oxidation of polyterpenes: Influence of the physical state, *Eur. Polym. J.*, **36**(10), 2000, 2133–2142.

98. Blazquez C.H., Vidyarth A.D., Sheehan T.D., Bennett M.J., McGrew G.T., Effect of pinolene (beta-pinene polymer) on carbaryl foliar residues, *J. Agric. Food Chem.*, **18**(4), 1970, 681–684.

99. Vippa P., Rajagopalan H., Thakur M., Electrical and optical properties of a novel nonconjugated conductive polymer, poly(beta-pinene), *J. Polym. Sci. B: Phys.*, **43**(24), 2005, 3695–3698.

100. Rajagopalan H., Vippa P., Thakur M., Quadratic electro-optic effect in a nano-optical material based on the nonconjugated conductive polymer, poly(beta-pinene), *Appl. Phys. Lett.*, **88**(3), 2006.

101. Yang M.C., Perng J.S., Camphene as a novel solvent for polypropylene: Comparison study based on viscous behavior of solutions, *J. Appl. Polym. Sci.*, **76**(14), 2000, 2068–2074.

102. Yang M.C., Perng J.S., Comparison of solvent removal methods of microporous polypropylene tubular membranes via thermally induced phase separation using a novel solvent: Camphene, *J. Polym. Res. Taiwan*, **6**(4), 1999, 251–258.

103. Yang M.C., Perng J.S., Microporous polypropylene tubular membranes via thermally induced phase separation using a novel solvent – Camphene, *J. Membr. Sci.*, **187**(1–2), 2001, 13–22.

104. Bjerknes K., Sontum P.C., Smistad G., Agerkvist I., Preparation of polymeric microbubbles: Formulation studies and product characterisation, *Int. J. Pharm.*, **158**(2), 1997, 129–136.
105. Bjerknes K., Dyrstad K., Smistad G., Agerkvist I., Preparation of polymeric microcapsules: Formulation studies, *Drug Dev. Ind. Pharm.*, **26**(8), 2000, 847–856.
106. Bjerknes K., Braenden J.U., Smistad G., Agerkvist L., Evaluation of different formulation studies on air-filled polymeric microcapsules by multivariate analysis, *Int. J. Pharm.*, **257**(1–2), 2003, 1–14.
107. Huang Y.B., Gao L.X., Ding M.X., Polymerization of styrene oxide catalyzed by a diethylzinc/alpha-pinene oxide system, *J. Polym. Sci. A: Polym. Chem.*, **37**(24), 1999, 4640–4645.
108. Shin C.Y., Chase G.G., Nanofibers from recycle waste expanded polystyrene using natural solvent, *Polym. Bull.*, **55**(3), 2005, 209–215.
109. Mathers R.T., McMahon K.C., Damodaran K., Retarides C.J., Kelley D.J., Ring-opening metathesis polymerizations in D-limonene: A renewable polymerization solvent and chain transfer agent for the synthesis of alkene macromonomers, *Macromolecules*, **39**(26), 2006, 8982–8986.
110. Di Lorenzo M.L., Cimmino S., Silvestre C., Nonisothermal crystallization of isotactic polypropylene blended with poly(alpha-pinene). 2. Growth rates, *Macromolecules*, **33**(10), 2000, 3828–3832.
111. Di Lorenzo M.L., Cimmino S., Silvestre C., Nonisothermal crystallization of isotactic polypropylene blended with poly(alpha-pinene). I. Bulk crystallization, *J. Appl. Polym. Sci.*, **82**(2), 2001, 358–367.
112. Di Lorenzo M.L., Spherulite growth rates in binary polymer blends, *Prog. Polym. Sci.*, **28**(4), 2003, 663–689.

– 3 –

Materials from Vegetable Oils: Major Sources, Properties and Applications

Mohamed Naceur Belgacem and Alessandro Gandini

ABSTRACT

This chapter summarizes the most recent advances in the realm of the modification of vegetable oils aimed at their use in the preparation of polymeric materials. After a brief description of the most important industrial oils, their major sources, their worldwide production, some of their properties and isolation procedures are reviewed. The contents are then divided into different sections, including the crosslinking of oils by vinyl monomers and by metal-catalyzed reactions, the formation of interpenetrating networks, the modification of epoxidized and castor oils and the polymerization of the resulting products. Subsequently, different oil-based polyurethanes, polyamides, polyester-amides, alkyd resins and polyesters and poly(hydroxyalkanoates) are reviewed. With each family of oil-based polymers, the most promising materials and their relevant properties are singled out stressing their suitability to replace, at least partially, petroleum-based counterparts.

3.1 INTRODUCTION

Vegetal and animal oils and fats have been used for centuries in the production of coatings, inks, plasticizers, lubricants and agrochemicals, as reported in recent books and reviews [1–5]. As expected, this scientific literature is largely complemented by a wide range of patents [6–12]. In 2000, the production of oils and fats amounted to 17.4 kg per year per capita and it is estimated that these figures grow at a rate of 3.3 per cent per year. The total worldwide yearly production of these renewable materials was over 110 million tons in 2002. Vegetal oils constitute the main fraction of this production (*i.e.* 80 per cent, the remaining 20 per cent being animal fats). Only 15.6 million tons (around 15 per cent) of these raw materials are used as precursors to the synthesis of new chemical commodities and materials. The rest is used for animal (about 5 per cent) and human (*ca*. 80 per cent) consumption.

The main actors involved in oleochemistry are located in Asia, because of the climatic suitability for such agricultural activity: Malaysia, Indonesia and the Philippines being the main producers. Fats from animal biomass are produced mostly in the US and Europe. The respective production of fats and oils for the four main continents, Asia, North America, Europe and South America, is 44, 16, 15 and 14 per cent. The present chapter deals exclusively with the use of vegetable oils as sources of polymeric materials, because the structures of fats do not lend themselves meaningfully to that application.

Table 3.1

Average annual worldwide production of 17 commodity oils,
for 2001–2005 period [1]

Oil	Average annual production (million tons)	Main producer
Soybean	26.52	US
Palm	23.53	Malaysia
Rapeseed/canola	15.29	Europe
Sunflower	10.77	Europe
Tallow	8.24	US
Lard	6.75	China
Butterfat	6.26	Europe
Groundnut	5.03	China
Cottonseed	4.49	China
Coconut	3.74	Philippines
Palm kernel	2.95	Malaysia
Olive	2.52	Europe
Corn	2.30	US
Fish	1.13	Peru
Linseed	0.83	Europe
Sesame	0.76	China
Castor	0.56	India
Total	**121.67**	
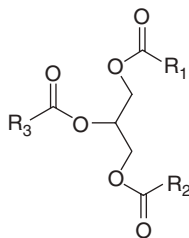
Where: R_1, R_2 and R_3 are fatty acid chains.

Scheme 3.1

Vegetal oils can be extracted from different species, as summarized in Table 3.1, which gives the average annual worldwide production of the 17 most important commodity oils. The major growth in the vegetable oil production is presently related to palm and rapeseed/canola oil [1].

As a general rule, the chemical composition of oils arises from the esterification of glycerol with three fatty acid molecules, as shown in Scheme 3.1. A given oil is always made up of a mixture of triglycerides bearing different fatty acid residues. The chain length of these fatty acids can vary from 14 to 22 carbons and contain 0–5 double bonds (DB) situated at different positions along the chain and in conjugated or unconjugated sequences. Table 3.2 collects the 16 most important oils with their specific chemical structures. Interestingly, none of them incorporated conjugated DB, which are however encountered in other less abundant oils.

In terms of chemical structure, few exceptions should be mentioned, since some fatty acids bear other types of functional groups, mainly epoxy rings and hydroxy moieties, triple bonds and ether functions [5], as discussed below. The fatty acid content in several common oils is given in Table 3.3 which, in addition, also provides the average number of DB per triglyceride unit. In the case of the more exotic castor, oiticica and tung oils, the main fatty acid residues are ricinoleic (87.5 per cent), licanic (74 per cent) of α-elaeostearic acids (84 per cent), respectively whose structures are provided in Scheme 3.2 below.

Alkyd resins are probably among the oldest polymers prepared from renewable resources through the esterification of polyhydroxy alcohols with polybasic and fatty acids. A considerable amount of technological research has

Table 3.2

Names and double bond positions of the most common fatty acids [1]

Chain length: Number of DB	Systematic name	Trivial name	Double bond position
12:0	Dodecanoic	Lauric	–
14:0	Tetradecanoic	Myristic	–
16:0	Hexadecanoic	Palmitic	–
18:0	Octadecenoic	Stearic	–
18:1	9-Octadecanoic	Oleic	9
18:2	9,12-Octadecadeinoic	Linoleic	9,12
18:3	6,9,12-Octadecatrienoic	γ-linolenic	6,9,12
18:3	9,12,15-Octadecatrienoic	α-linolenic	9,12,15
20:0	Eicosanoic	Arachidic	–
20:1	Eicosaenoic	–	9
20:4	Eicosatetraenoic	Arachidonic	5,8,11,14
20:5	Eicosapentaenoic	EPA	5,8,11,14,17
22:0	Docosanoic	–	–
22:1	Docosenoic	Erucic	13
22:5	Docosapentanoic	DPA	7,10,13,16,19
22:6	Docosahexanoic	DHA	4,7,10,13,16,19

Table 3.3

Main fatty acid contents in different oils [2, 13]

Oils	Fatty acid					Average number of DB per triglyceride
	Palmitic	Stearic	Oleic	Linoleic	Linolenic	
Canola	4.1	1.8	60.9	21.0	8.8	3.9
Corn	10.9	2.0	25.4	59.6	1.2	4.5
Cottonseed	21.6	2.6	18.6	54.4	0.7	3.9
Linseed	5.5	3.5	19.1	15.3	56.6	6.6
Olive	13.7	2.5	71.1	10.0	0.6	2.8
Soybean	11.0	4.0	23.4	53.3	7.8	4.6
Tung	–	4.0	8.0	4.0	–	7.5
Fish	–	–	18.20	1.10	0.99	3.6
Castor	1.5	0.5	5.0	4.0	0.5	3.0
Palm	39	5	45	9	–	–
Oiticica	6	4	8	8	–	–
Rapeseed	4	2	56	26	10	–
Refined tall	4	3	46	35	12	–
Sunflower	6	4	42	47	1	–

been devoted to the properties of these polyesters and the interested reader will find much detailed information in a monograph entirely devoted to them [14]. Here, we limit our coverage to the most relevant findings in the field of alkyd resins as polymeric materials.

3.2   PROPERTIES OF VEGETABLE OILS AND FATTY ACIDS

The physical and chemical properties of vegetable oils depend on their fatty acid distribution. The numbers of DB, as well as their positions within the aliphatic chain, affect strongly the oil properties. The actual number of carbon

Table 3.4

Some physical properties of triglyceride oils and fatty acids [15]

Name	Viscosity (mPa·s)	Specific gravity	Refractive index	Melting point (°C)
Castor oil	293.4 at 37.8°C	0.951 at 20°C	1.473–1.480 at 20°C	−20 to −10
Linseed oil	29.6 at 37.8°C	0.925 at 20°C	1.480–1.483 at 20°C	−20
Palm oil	30.92 at 37.8°C	0.890 at 20°C	1.453–1.456 at 20°C	33–40
Soybean oil	28.49 at 37.8°C	0.917 at 20°C	1.473–1.477 at 20°C	−23 to −20
Sunflower oil	33.31 at 37.8°C	0.916 at 20°C	1.473–1.477 at 20°C	−18 to −16
Myristic acid	2.78 at 110°C	0.844 at 80°C	1.4273 at 70°C	54.4
Palmitic acid	3.47 at 110°C	0.841 at 80°C	1.4209 at 70°C	62.9
Stearic acid	4.24 at 110°C	0.839 at 80°C	1.4337 at 70°C	69.6
Oleic acid	3.41 at 110°C	0.850 at 80°C	1.4449 at 60°C	16.3

Table 3.5

Iodine values of some unsaturated fatty acids and their triglycerides

Fatty acid (number of carbon atoms)	Iodine value of the	
	Acid	Triglyceride
Palmitoleic (C16)	99.8	95.0
Oleic (C18)	89.9	86.0
Linoleic (C18)	181.0	173.2
Linolenic (C18) and α-eleostearic	273.5	261.6
Ricinoleic (C18)	85.1	81.6
Licanic (C18)	261.0	258.6

atoms making up the aliphatic chains plays a very minor role, simply because most of these triglycerides have 18 and a few 16. Table 3.4 summarizes some relevant properties of common vegetable oils and fatty acids. The average degree of insaturations is measured by the iodine value. This parameter corresponds to the amount of iodine (mg) which reacts with the DB in 100 g of the oil under investigation. Vegetable oils are divided into three groups depending on their iodine values. Thus, oils are classified as 'drying', if their iodine value is higher than 130, 'semi-drying' if this parameter is comprised between 90 and 130 and 'non-drying' when it drops below 90. Iodine values of some common fatty acids and their triglycerides are given in Table 3.5.
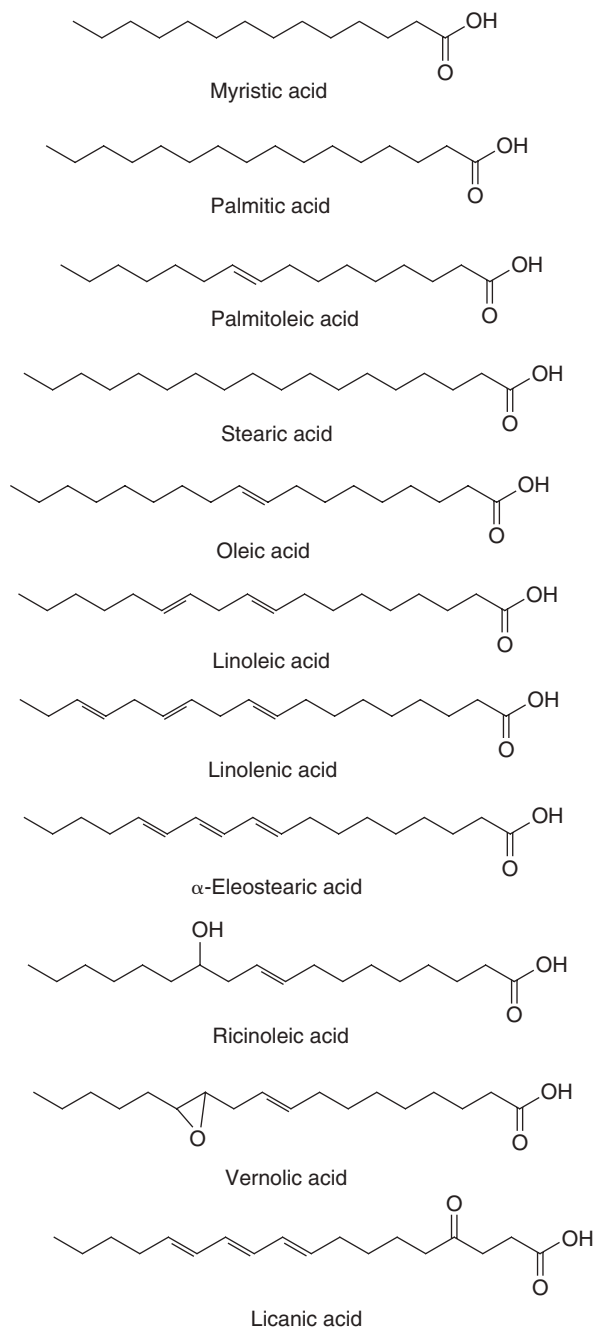
3.3   ISOLATION OF VEGETABLE OILS

The isolation of vegetable oils can be achieved either mechanically or by solvent extraction [16]. The mechanical process consists of submitting the beans, cells and oil bodies to shearing, in order to liberate the oil. Heat is generated during this procedure and this can induce a negative effect on the proteins therein. The advantages of the mechanical isolation process reside in its low cost, low investment and safety in terms of environmental concerns, since it does not involve the use of solvents or hazardous substances. This process presents, nevertheless, the drawback of low yields of oil extraction, since the amount of oil left in the ensuing residues can reach values as high as 7 per cent.

The main principle of solvent extraction is that the solvent diffuses through the seeds, solubilizes and extracts the oil. Solvent extraction involves the use of organic solvents, the most common being hexane. The key parameter of this process is the diffusion rate of the solvent into the oil body. This process is more efficient than the mechanical counterpart, but has the drawback of using volatile organic solvents.

3.4 POLYMERS FROM VEGETABLE OILS

Soybean, fish, corn, tung, linseed and castor oils are the most common renewable resources used as precursors for the synthesis of vegetable oil-based polymers. Their composition in fatty acid is shown in Table 3.3 [3, 17]. The chemical structures of the most representative oils in these families are given in Scheme 3.2.

Myristic acid

Palmitic acid

Palmitoleic acid

Stearic acid

Oleic acid

Linoleic acid

Linolenic acid

α-Eleostearic acid

Ricinoleic acid

Vernolic acid

Licanic acid

Scheme 3.2

The free radical oxido-polymerization of unsaturated triglycerides in atmospheric conditions has been (and continues to be) exploited mostly in coating applications involving inks and paints. These systems and the mechanisms they involve represent well-established and well-documented traditional processes [15–17] and will not be discussed any further here, also because, in terms of bulk material properties, the ensuing networks display rather poor mechanical properties.

Other chemical exploitations of these molecules as macromonomers are instead becoming particularly promising, whether they involve reactions with the DB, the hydroxy groups or epoxy functions borne by some of their structures. Since this topic was covered by two very recent reviews [2, 3] and two books [1, 4], we will confine ourselves here to reviewing relevant studies in the field of macromolecular architecture with an emphasis on the potential viability of these novel materials derived from renewable resources. Of course, more recent contributions will also be assessed.

3.4.1 Crosslinking of oils by vinyl monomers

Linseed (**LO**), tung (**TO**), soybean (**SOYO**), fish (**FO**), sunflower (**SFO**), corn (**CORO**), oiticica (**OTO**) and dehydrated castor oils (**DCO**) are relatively DB rich molecules, which makes them suitable for copolymerization with vinyl monomers, such as styrene (**ST**), α-methyl styrene (**MST**), divinyl benzene (**DVB**) or cyclopentadiene (**CPD**). These oils have thus been used to produce polymeric networks through their copolymerization with vinyl monomers by the so-called grafting-through mechanism. The **SOYO** used for the preparation of polymeric materials is available in three grades, namely (i) regular, (ii) low saturated non-conjugated and (iii) conjugated saturated. The fatty acids which constitute **SOYO** are mainly C18 and the number of DB is about five per triglyceride molecule, as shown in Table 3.3. Two varieties of **SOYO** are available on the market, viz. non-modified and epoxidized (**ESOY**). **ESOY** can be submitted to further modifications, such as esterification or urethane formation, as described in the appropriate section below.

Regular **SOYO**, **LO**, **CORO**, **TO** and **FO** oils were extensively studied by Larock *et al*. [18–34], who submitted them to cationic copolymerization with vinyl monomers in the presence of boron trifluoride diethyl etherate (**BFE**), as initiator. Thus, native Norwegian and conjugated **FO**, as well as conjugated and non-conjugated **FO** ethyl esters, were submitted to copolymerizations with **ST**, **DVB**, **DCP** and **NBD**, in various combinations and proportions, and the ensuing thermosets characterized in terms of structures and mechanical properties [18, 19, 24, 26]. The glass transition temperatures of these materials varied from 11°C to 113°C, as a function of the monomer combination and composition. Generally, conjugated oils gave stiffer thermosets. The free oil, the gel fraction and the amount of incorporated oils varied from 15 to 32 per cent, 41 to 85 per cent and 30 to 50 per cent, respectively. As expected, the gel fraction of these materials exhibited a higher thermal stability. Some other comonomers were also tested with both conjugated and non-conjugated **FO** ethyl esters, namely furfural, *p*-benzoquinone, *p*-mentha-1,8-diene, furan, the Diels–Alder adduct between furfural and *p*-mentha-1,8-diene, maleic anhydride and vinyl acetate. The aim of these investigations was to modulate the glass transition temperature of the ensuing products.

SOYO alone, or in combination with other oils, was also studied in the context of cationic copolymerizations with the same comonomers mentioned above [20–23, 25, 27–29, 32, 33]. The **SOYOs** used were low saturated (**LSO**) or conjugated low saturated soybean (**CLS**) oils and the cationic initiator was blended with **FO**. The formulation of **TO** and **LSO** oils gave highly crosslinked networks with **ST** and **DVB** (95–96 per cent). **CORO** was also copolymerized with **ST** and **DVB** using **BFE**. The resulting copolymers were characterized by dynamic and thermal mechanical analysis (DMA and TMA), thermogravimetry (TGA), differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). The gelation time in these very different systems varied from a few minutes to a few days. The Tgs and the moduli of the prepared copolymer varied from 0°C to 105°C and from 6 to 2 000 MPa, respectively. These values are comparable to those of commercial rubbers synthesized from petroleum-based monomers. The free oil, the gel fraction and the amount of incorporated oils varied from, 12 to 27 per cent, 69 to 88 per cent and 29 to 56 per cent, respectively. These oil-based thermosets started to be degraded at temperatures higher than 400°C. Their toughness reached 4 MPa, for some combinations. The shape memory effect of these materials was also studied. It consisted in the establishment of three parameters, namely (i) their deformability (D) behaviour at temperatures higher than their Tg, (ii) the degree to which the deformation is subsequently fixed at ambient temperature (FD) and (iii) the final shape recovery (R) when the

sample is reheated. Crosslinked samples with Tgs well above the ambient temperature exhibited good shape memory effects.

Very recently, novel thermosetting copolymers were prepared from **SOYO** and dicyclopentadiene (**DCP**) [32] using the catalytic system. The ensuing materials varied from tough and ductile to very soft rubbers. The gel fraction varied between 69 and 88 per cent and the Tgs were in the range of −20°C to 40°C. These materials lost 10 per cent of their weight at temperatures around 330°C. In the same vein, nanocomposites based on **SOYO**-**ST** and **SOYO**-**DVB** matrices reinforced with a reactive organo-modified montmorillonite clay were also prepared and showed, as expected, better mechanical properties and improved thermal resistance, compared with their respective matrices [33].

TO and **LO** were also tested in the same context [30, 31, 34] but the crosslinking was induced by a free radical mechanism using bezoyl- and *ter*-butylhydro-peroxides as well as azobisisobutyronitrile (AIBN), in the presence of acrylonitrile, **ST** and **DVB**. The onset of network formation occurred just above 140°C and fully crosslinked materials were obtained by post-curing at 160°C. The Tgs of these networks varied from 0°C to 110°C and the gel fraction reached 96 per cent for some combinations. The compressive modulus varied from 0.02 to 1.2 GPa, whereas the compressive strength ranged from 8 to 140 MPa. These materials were stable up to 300°C.

3.4.2 Crosslinking of modified oils by vinyl monomers

Castor oil (**CO**) and **LO** were reported to crosslink with **ST** in the presence of benzoyl peroxide, after being modified with acrylic acid (**AA**) through an inter-transesterification reaction [35].

The free radical crosslinking of bacterial polyesters obtained from **SOYO** has also been reported [36]. Thus, poly(-3-hydroxy octanoate) containing unsaturated side chains (**PHA–SOYO**) were produced from **SOYO** in the presence of *Pseudomonas oleovorans*. Subsequently, **PHA–SOYO** adducts were crosslinked, thermally or under UV irradiation, in the presence of a free radical initiator and ethylene glycol dimethacrylate as the crosslinker. The network yield reached 93 per cent and the Tg of the biopolyester increased from −60°C to −40°C after crosslinking.

SFO and **LO** were also styrenated after their transesterification with methyl methacrylate (**MMA**) in the presence of benzoyl peroxide [37] and the ensuing materials were characterized in terms of drying time, alkali and acid resistance and hardness. A more recent study reported the modification of **SOYO** and **SFO** by acrylamide derivatives [38] calling upon the use of Ritter's reaction. This rather fundamental study was limited to the determination of the reactivity ratios between **ST** and the different moieties of acrylamide derivatives.

Epoxynorborene derivatives of **LO** (see Scheme 3.3) were prepared and crosslinked by UV irradiation in the presence of tetraethylorthosiloxane (**TEOS**), in order to produce organic–inorganic hybrid films using (4-octyloxyphenyl) phenyl iodonium hexafluoroantimonate as the cationic photoinitiator [39]. Different formulations were studied, but in all cases the modified **LO** was in a large excess. The addition of 10 per cent of **TEOS** was found to be optimal in terms of the mechanical and adhesion properties of the composite films.
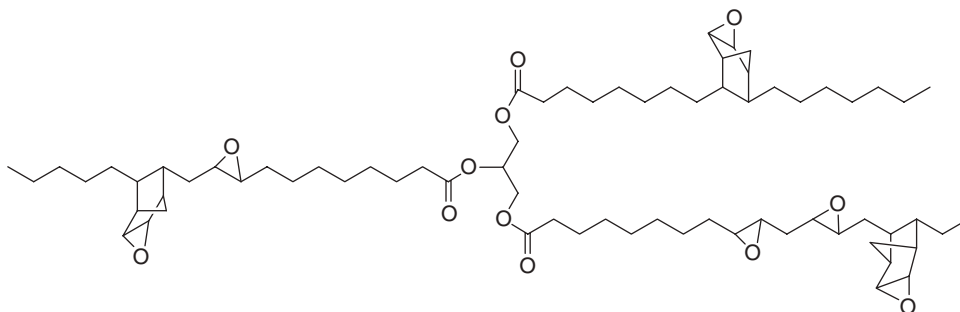

Scheme 3.3
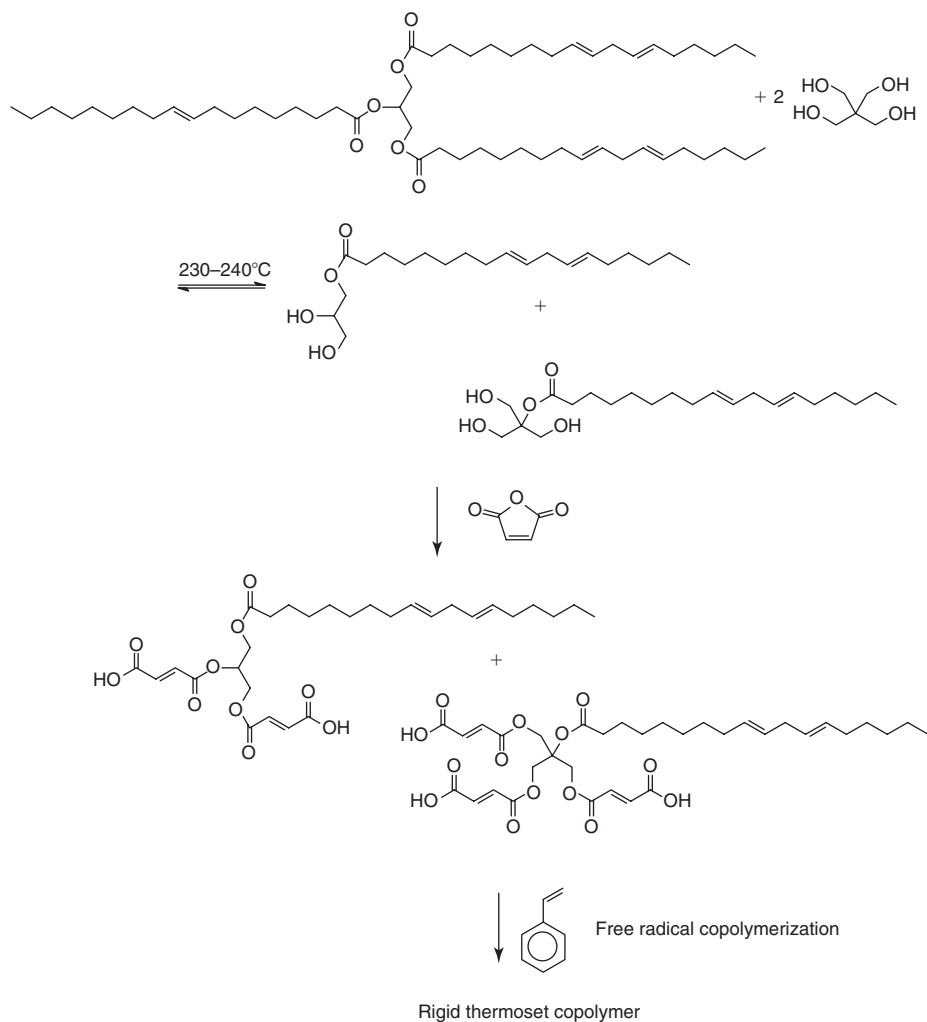
Scheme 3.4

SOYO and **CO** were also submitted to alcoholysis with pentaerythritol or biphenol-A propoxylate and the ensuing mixtures reacted with maleic anhydride before crosslinking with **ST** [40, 41], as sketched in Scheme 3.4 for **SOYO**. For **CO,** the grafting of maleic anhydride is more favoured, since **CO** contains 3-OH functions per triglyceride molecule. The modified oils were carefully characterized by NMR spectroscopy, as shown in Fig. 3.1.

The crosslinking was followed by FTIR spectroscopy which showed that about 1 h was needed to reach a high gel fraction. Total conversion was attained after 3 h at 120°C. The **SOYO**-based polymers exhibited flexural moduli and strength in the range of 0.8–2.5 GPa and 32–112 MPa, respectively. Their glass transition temperatures varied from 72°C to 150°C. The surface hardness of the **SOYO**-crosslinked networks varied between 77 D and 90 D. **CO**-based thermosetting materials exhibited significantly improved moduli, strengths and Tg values, when compared with **SOYO**-based counterparts. These novel materials, based on renewable vegetable oils, show properties comparable to those of high performance unsaturated polyester resins which make them good candidates to replace those petroleum-based products.

3.4.3 Crosslinking of virgin oils by metal-catalyzed reactions

LO was submitted to auto-oxidative crosslinking in the presence of different metal-based catalysts [42–44], viz. titanium (IV) i-propoxide, titanium di-i-propoxide bis(acetylacetonate), cobalt, lead and zirconium-octonoates,
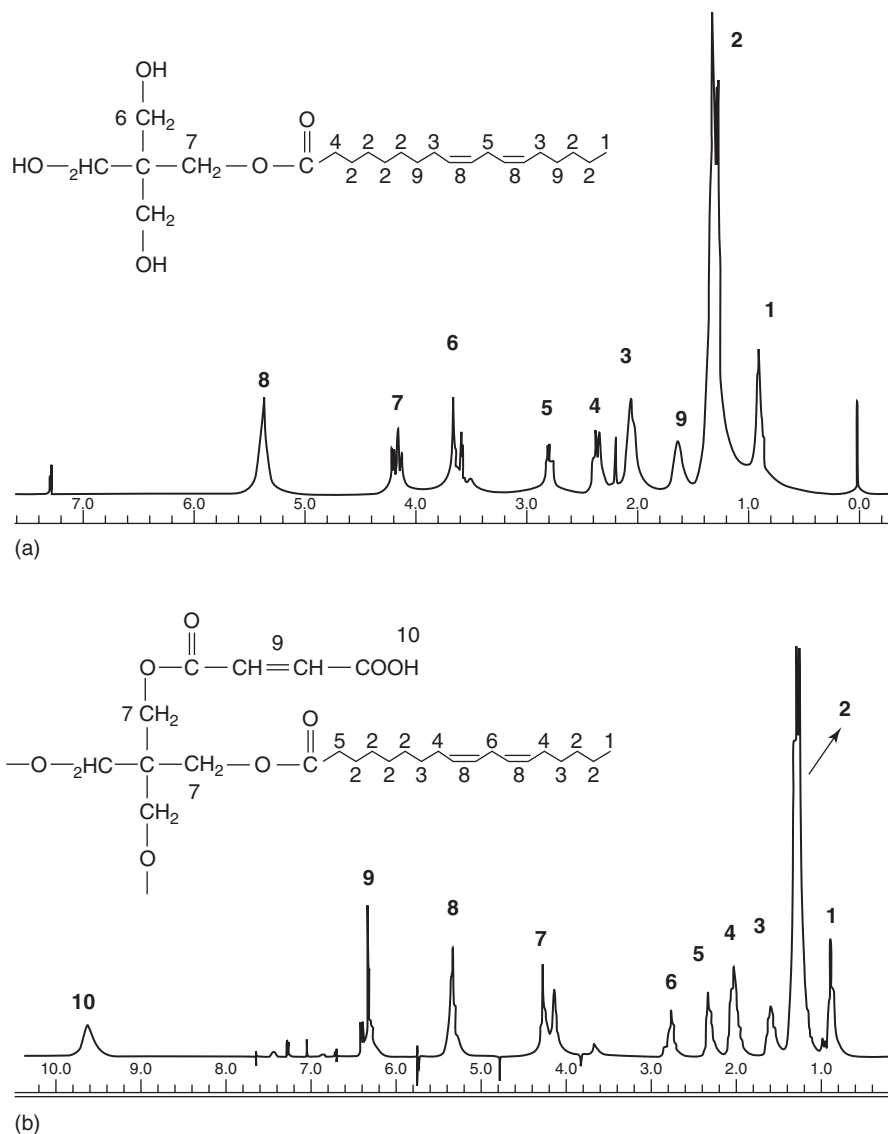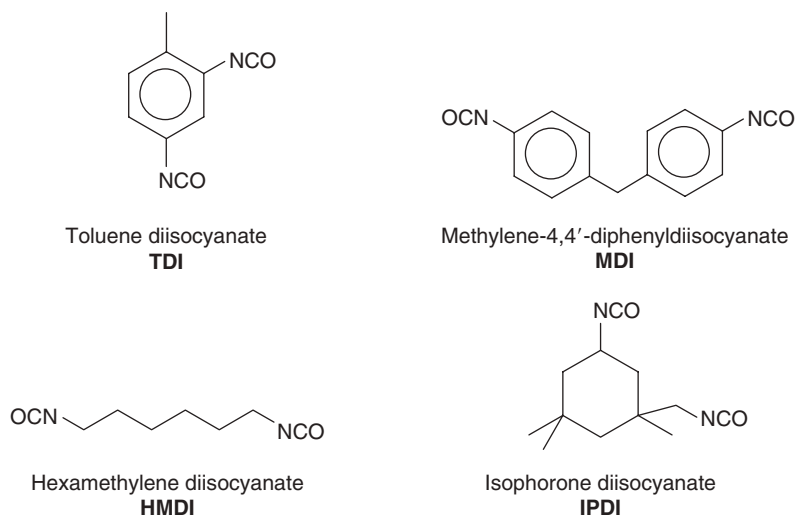
Figure 3.1 ^{1}H-NMR spectra of pentaerythritol-modified **SOYO** (a) and its maleic anhydride adduct (b). (Reproduced by permission of Wiley Periodicals, Inc. Copyright 2006. Reprinted from Reference [40].)

lead oxides and salts and iron oxides. The crosslinking reactions were followed by DSC. The increase in the amount of the catalyst induced a decrease in the heat of the reaction and increased the hardness of the crosslinked films. Cobalt salts were found to catalyse the oxidation step, whereas lead and zirconium homologues catalysed the polymerization reactions. The interest of these otherwise conventional systems lies solely in the purported possibility of replacing some toxic catalysts with environment-friendly counterparts, a claim which requires confirmation.

3.4.4 Crosslinking of modified oils forming interpenetrating networks

CO as such, after hydrogenation (**HCO**), or trans-esterification with glycerol, or modification with **LO**, or in combination with polyethylene glycol, were extensively used as precursors in the preparation of interpenetrating networks,

Toluene diisocyanate
TDI

Methylene-4,4′-diphenyldiisocyanate
MDI

Hexamethylene diisocyanate
HMDI

Isophorone diisocyanate
IPDI

Scheme 3.5

as recently reported [45–48] and reviewed [2]. The first step of this process consisted in the preparation of a poly-urethane component which involved the use of different isocyanates, as summarized in Scheme 3.5. The most commonly used vinyl and acrylic monomers were **ST**, **DVB**, alkyl acrylates and methacrylates, **AA**, acrylonitrile, ethylene glycol dimethacrylate and 2-hydroxyethyl methacrylate. These systems will not be described at length here since the reader will readily find more details in the cited references [2, 45–48].

3.4.5   Modification of epoxidized oils and polymerization of the resulting products

Crivello's group has been involved in the cationic polymerization of epoxidized triglycerides like vernonia, lesquer-ella, crambe, rapeseed, canola, **SOYO**, **SFO** and meadowfoam [49–52]. Two routes were applied for the epoxi-dization, (i) glacial acetic acid in the presence of hydrogen peroxide and (ii) phase-transfer catalyzed by methyl octylammonium (diperoxotungsto)phosphate. In all cases, the optimal conditions yielding a high conversion were established. Glass-fibre reinforced composite materials, in which these epoxidized oils were used as matrix-precur-sors, were also prepared and characterized.

Polymer networks derived from the curing of epoxidized **LO** have also been prepared and characterized [53]. The crosslinking agents were phthalic (**PA**), tetrahydro phthalic (**TPA**), tetrahydromethyl phthalic (**TMPA**), hexahy-dromethyl phthalic (**HMPA**) and methyl endomethylene tetrahydrophthalic (**MTPA**) anhydrides and the reaction was catalyzed by different tertiary amines. The effect of the steric hindrance and stiffness of the hardeners was also studied.

**TPA**   **TMPA**   **HMPA**   **MTPA**
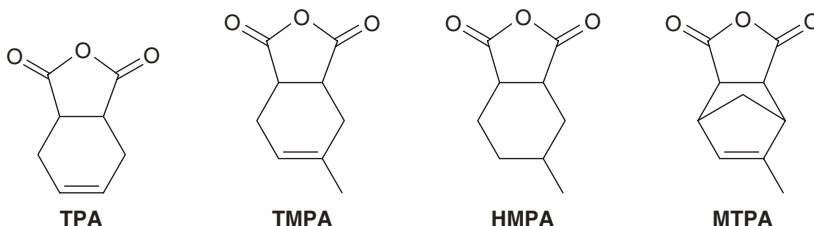
More recently, bromo-acrylated triglycerides were prepared from **SFO** and **SOYO** and the ensuing modified **SOYO** was homo-polymerized or co-polymerized with **ST** by free radical initiation [54]. This study was carried out with the aim of using the ensuing materials in the field of flame-resistant polymers. The FTIR, NMR and mass spectra of the bromo-acrylated methyl oleate were recorded and showed that the modification had been successful. **SOYO** gave a higher acrylate substitution than **SFO**. The glass transition temperatures of the polymers obtained were around 60 and 25°C, for **SFO**- and **SOYO**-based materials, respectively. These materials did indeed show good flame resistance [54].

CO was used in combination with a polyamide system in the preparation of coating adhesives [55] and some of these formulations showed excellent adhesion properties, satisfactory flexibility and good resistance to several chemicals. Epoxidized **CO** (**DECO**) were blended with **PMMA** in 80/20, 60/40 and 20/80 weight ratios, but these mixtures showed a certain degree of incompatibility [56, 57]. It follows that the possible application or copolymerization of these materials does not seem promising.

UV curable cycloalphatic epoxides were prepared from **LO** (**ELO**), as sketched in Scheme 3.6 and thoroughly characterized by FTIR, NMR and GPC. **ELO** was then efficiently UV cured and the conversion of the epoxy ring followed by monitoring the FTIR peak intensity at $831\,cm^{-1}$ [58]. Bio-based epoxy resins have been prepared by thermal cationic initiation using *N*-benzylpyrazinium hexafluoroantimonate (**BPH**) and *N*-benzylquinoxalinium hexafluoroantimonate (**BQH**) [59] and gave Tgs of 30–40°C. The mechanical properties of the films prepared by **BQH**-initiation were higher than those of the **BPH** counterpart, a fact which was attributed to the higher crosslink density reached with the former system.
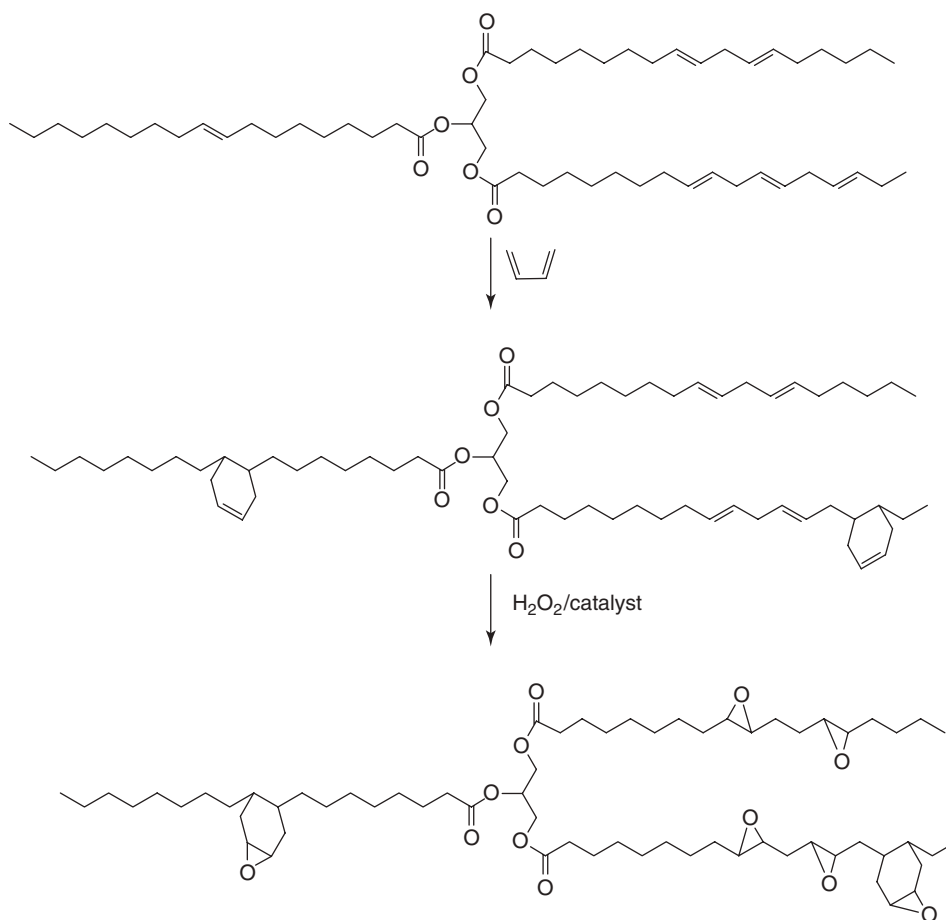

Scheme 3.6

More recently, a commercial sample of epoxidised **SOYO** (**ESOYO**) was thoroughly characterized [60–62], before being submitted to different modifications. The FTIR spectrum of **ESOYO** is given in Fig. 3.2, which shows the characteristic ester bands at $1743\,cm^{-1}$ (carbonyl groups, C=O) and at $1159\,cm^{-1}$ (ester moieties C—O), together with the oxirane peak at $823\,cm^{-1}$. The ^{1}H-NMR spectrum of **ESOYO** is presented in Fig. 3.3, and
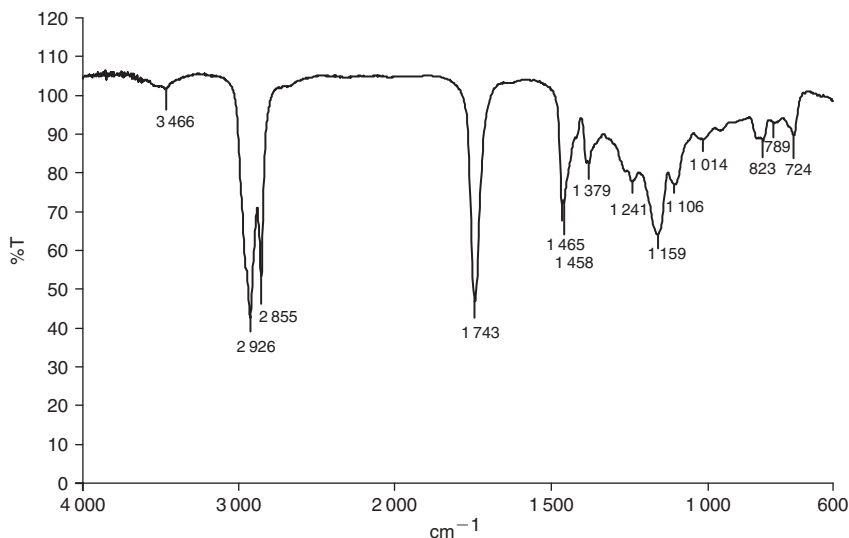

Figure 3.2   FTIR Spectrum of **ESOYO**, reported in reference [61]. (Reproduced by permission of the Wiley-VCH Verlag GmnH & Co. KGaA. Copyright 2006. Reprinted from Reference [61]).
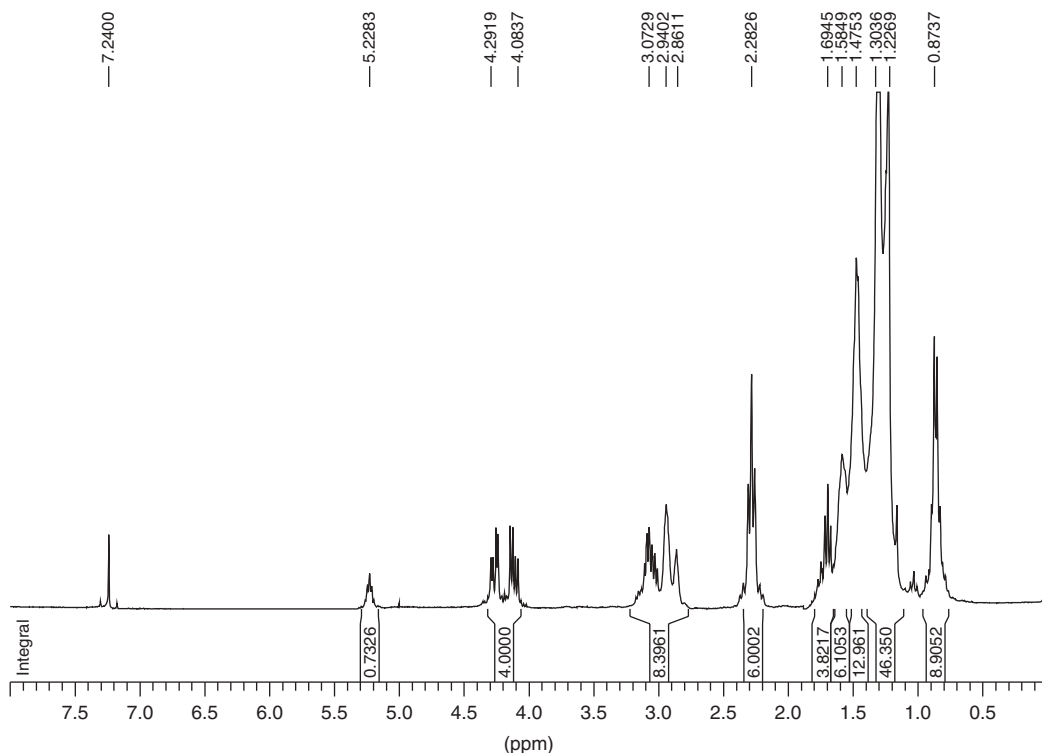
Figure 3.3 ^{1}H-NMR spectrum of **ESOYO** in CDCl$_3$ [60].

Table 3.6 summarizes its peak assignments. From this spectrum and the data presented in Table 3.6, the number of epoxy groups present in each triglyceride molecule was calculated. Thus, the intensity of the peaks between 2.9 ppm and 3.1 ppm, associated with epoxy functions, corresponded to 8.4 protons (*i.e.* about 4.5 oxirane moieties per molecule). This is in rather good agreement with the composition of **SOYO**, that is, on average, two linoleic and one oleic residues, as indicated in Table 3.3, which predicts the conversion of the five insaturations present in the initial triglyceride molecule into the corresponding oxirane function. The elemental analyses and the molecular weight determinations confirmed this structure.

   ESOYO was then modified by reactions with **AA** or acryloyl chloride and the acrylated derivatives characterized by spectroscopic techniques before being submitted to free radical photopolymerization. The NMR spectrum of the acrylated **ESOYO** (**AESOYO**) is shown in Fig. 3.4. Table 3.6 summarizes the peak assignments and their
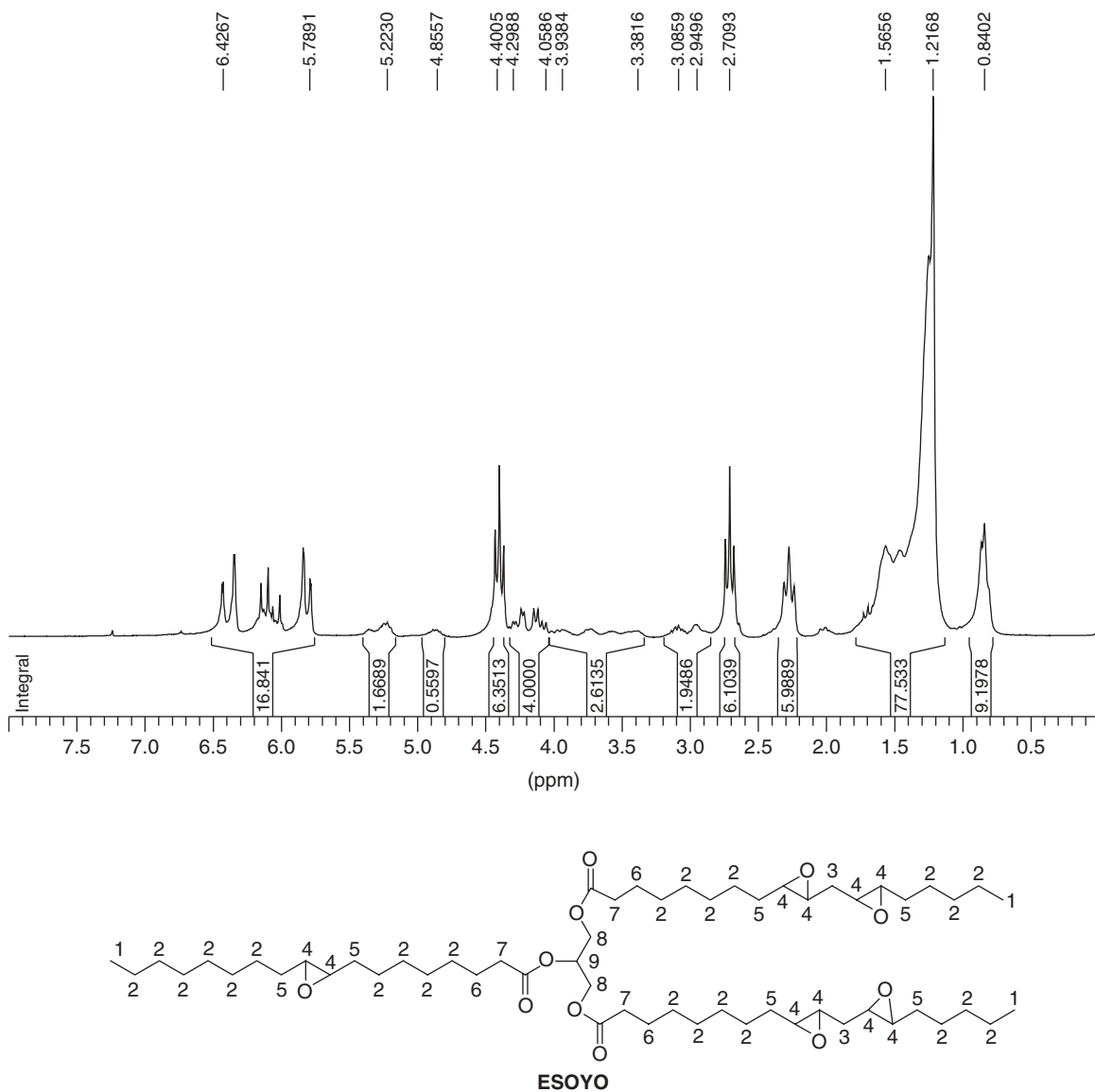
Figure 3.4   ¹H-NMR spectrum of **AESOYO** in CDCl₃ [60].
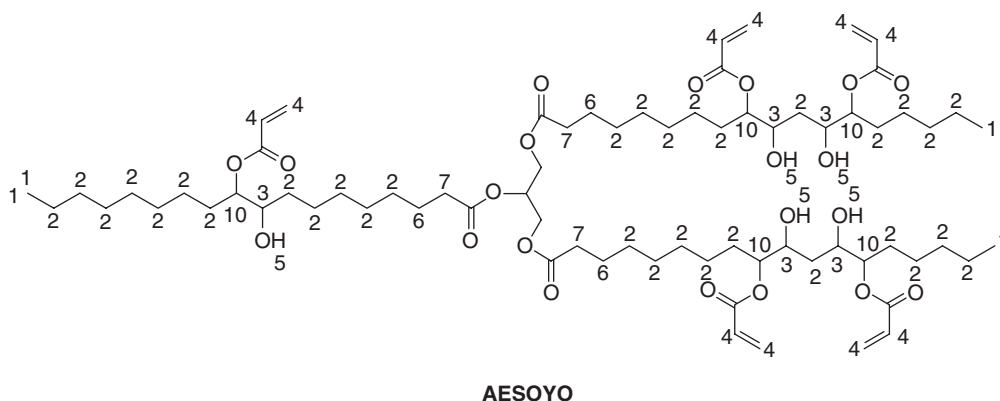
AESOYO

Figure 3.4   (*Continued*).

Table 3.6

^{1}H-NMR data relative to ESOYO [60]

ESOYO			AESOYO		
δ (ppm)	Intensity	Peak assignment	δ (ppm)	Intensity	Peak assignment
			5.8–6.4	16.8	H_4
5.2	1	H_9	5.2–5.3	1.6	H_9
4–4.3	4	H_8	4.3	6	H_{10}
2.9–3.1	8.4	H_4	4–4.3	4	H_8
2.3	6	H_7	3.4–4	2.6	H_5
1.7	4	H_3	2.9–3.1	2	H_{11}
1.6	6	H_6	2.7	6	H_3
1.5	13	H_5	2.3	6	H_7
1.3–1.4	46	H_2	1.3–1.6	77	H_6 and H_2
0.9	9	H_1	0.9	9	H_1

Figure 3.5   Evolution of the bands at $1\,637$ and $1\,627\,cm^{-1}$ in the FTIR spectra of **AESOYO** irradiated in solution in the presence of 4 per cent of Darocure $1\,173$ [60].

intensity. The irradiation of **AESOYO** was accompanied by FTIR spectroscopy in order to monitor the decrease of peak attributed to the C=C acrylic moieties, as shown in Fig. 3.5. This reaction rapidly generated a highly cross-linked network.

   Of two very recent additions to the present context, one concerns the crosslinking of both **ELO** and epoxidized synthetic triglycerides obtained from ω-unsaturated fatty acids with either 4,4'-methylene dianiline or **PA** [63]. Films of these materials were glassy, since their Tgs varied from about 50°C to 130°C, and stiffer than those pre-pared from conventional bisphenol A-diglycidyl ether (**BADGE**)-based epoxy resins. However, the adhesion and the shear strength of these oil-based resins were better than those of classical **BADGE**-based counterparts. The other recent contribution deals with the free radical photocopolymerizations of **ESOYO** and maleinized **ESOYO** (**MESOYO**) with **ST**, vinyl acetate and **MMA** [64]. The authors concluded that these copolymers could be good candidates for liquid moulding resins.

3.4.6   Modification of CO and polymerization of the resulting products

The castor oil employed in this investigation was an industrial product whose FTIR spectrum, shown in Fig. 3.6, displays bands characteristic of OH functions at $3401\,cm^{-1}$, carbonyl groups at $1745\,cm^{-1}$ and a weak peak at $3007\,cm^{-1}$ attributed to insaturations.
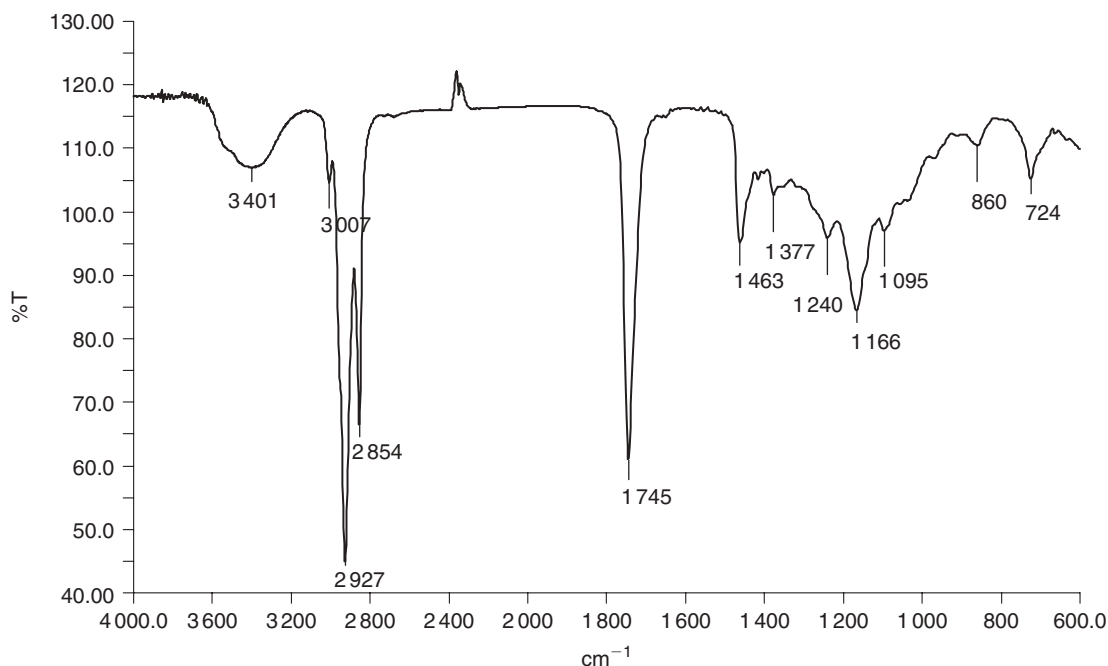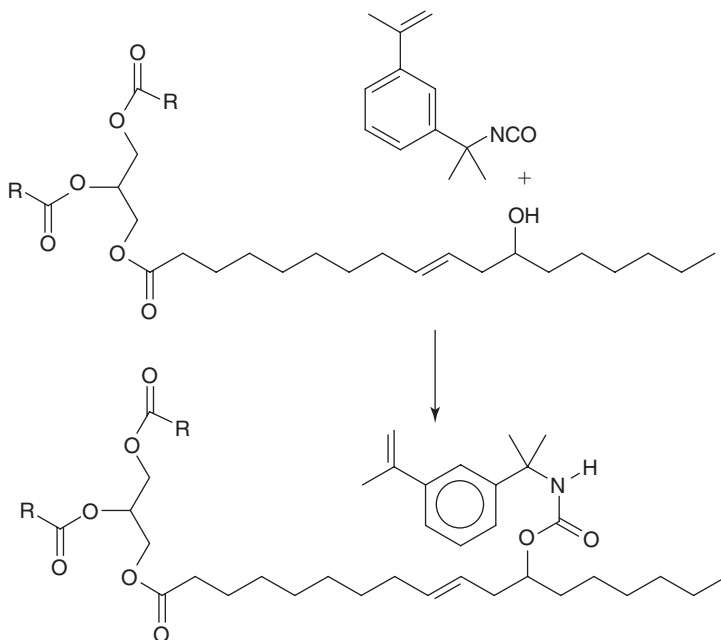

Figure 3.6   FTIR spectrum of industrial **CO**, reported in Reference [61]. (Reproduced by permission of the Wiley-VCH Verlag GmnH & Co. KGaA. Copyright 2006. Reprinted from Reference [61]).

   The ^{1}H-RMN spectrum given in Fig. 3.7 had all the resonances expected for the **CO** structure, viz. 3-hydroxy groups and 3 insaturations per triglyceride molecule. Additionally, elemental analyses and molecular weight deter-mination confirmed the proposed structure.
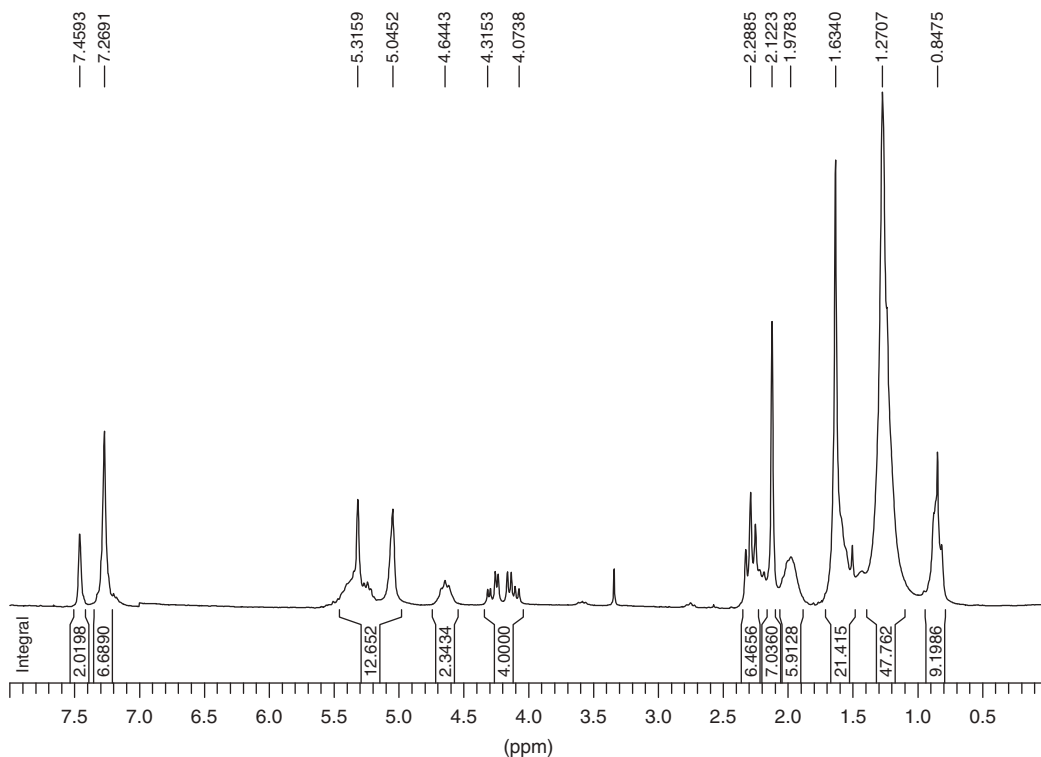
   CO was modified by reacting it with **AA**, acryloyl chloride (**AC**) and α,α'-dimethylbenzylisocyanate (**TMI**). The latter reaction is depicted in Scheme 3.7 and the FTIR and NMR spectra of the **CO-TMI** adduct are given
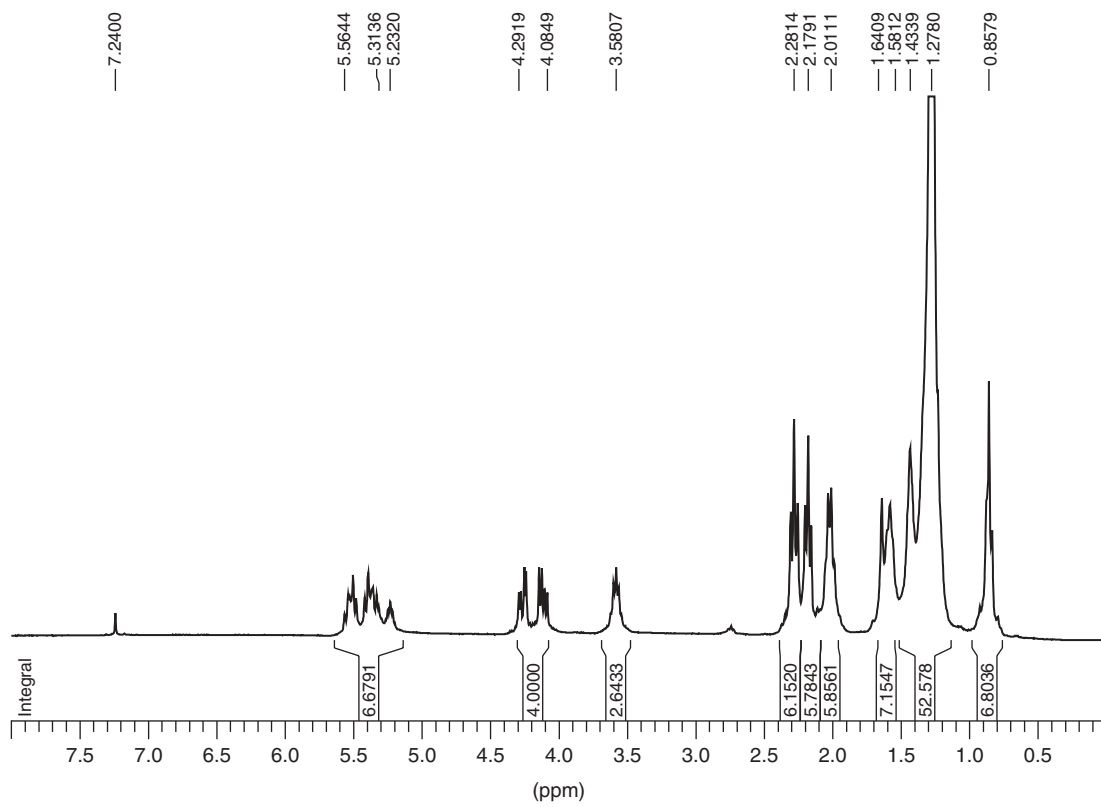
**Figure 3.7** ^{1}H-NMR spectrum of industrial **CO** in CDCl$_3$ [60].

Scheme 3.7

Figure 3.8 ^{1}H-NMR spectrum of **CO-TMI** in CDCl₃, reported in Reference [61]. (Reproduced by permission of the Wiley-VCH Verlag GmnH & Co. KGaA. Copyright 2006. Reprinted from Reference [61]).

in Figs 3.7 and 3.8, respectively, whereas Table 3.7 summarizes the NMR peak assignments for both **CO** and **CO-TMI**. The acrylated **CO** derivatives were found to crosslink via radical photopolymerization, whereas the **CO-TMI** adduct was crosslinked via cationic polymerization [60–62].
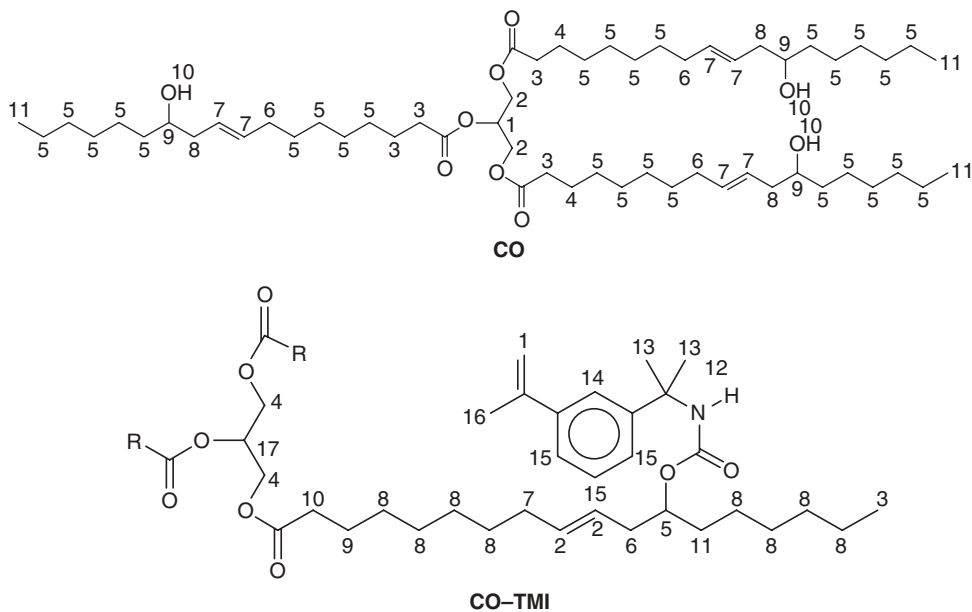
Table 3.7

^{1}H-NMR data relative to CO and CO–TMI [61]

| δ (ppm)	Intensity	Peak assignment	δ (ppm)	Intensity	Peak assignment
7.24	–	The solvent	7.4	2	H_{14}
5.2–5.5	6.6	H_1 and H_7	7.3	7	H_{15}
4–4.3	4	H_2	5–5.3	13	H_{17}, H_1 and H_2
3.6	2.6	H_{10}	4.6	2	H_5
2.3	6	H_3	4–4.3	4	H_4
2.2	6	H_8	2.3	6	H_{10}
2	6	H_6	2.1	9	H_{16}, H_6
1.6	7	H_4	2	6	H_7
1.3–1.4	53	H_5	1.6	21	H_{11} and H_{13}
0.8	7	H_{11}	1.3	48	H_9, H_8
			0.8	9	H_3

3.4.7 Oil-based polyurethanes

Thanks to their good film-forming properties, **LO** and **SFO** were tested in paint formulations after their submission to chemical modification. Thus, initial triglycerides or their partially hydrolysed derivatives were reacted with **TDI**, **HMDI** or an NCO-terminated pre-polymer between 1,4-butanediol and **TDI** [65–67]. The viscosity of the **TDI**-**SFO**-based polymer solutions showed a non-Newtonian rheo-thinning behaviour, whereas those of the other polymers behaved as Newtonian fluids. **CO**-based polyurethanes gave polymers with Tgs varying from 25°C to 50°C and a gel fraction higher than 90 per cent. Water soluble polyurethanes were obtained from **SFO**-based maleinized fatty acids [68] and **TDI** in the presence of tertiary amines as catalysts. The films obtained displayed good resistance to abrasion and to mechanical impacts and good gloss.

Very recently, novel silicon-containing polyurethanes based on vegetable oils were prepared and characterized [69]. In particular, a silicon-fatty acid OH-terminated triglyceride (Si-oil-polyol) (Scheme 3.8) was prepared and reacted with methylenediphenyl diisocyanate (**MDI**). This polyol was characterized by its hydroxy number, functionality, molecular weight and NMR (Fig. 3.9). The Tgs of the corresponding polyurethanes decreased when the proportion of Si-oil-polyol was increased. It was found that higher silicon contents yielded materials which no longer burned in ambient air in the absence of complementary oxygen, indicating that these hybrids can be potential candidates for applications that require fire resistance.

3.4.8 Oil-based polyamides

The study of polyamides prepared from vegetable oils is an old field of research which has not reported any new data in the last three decades. Polyamides from **TO** and **SOYO** were used mainly in the paint industry because
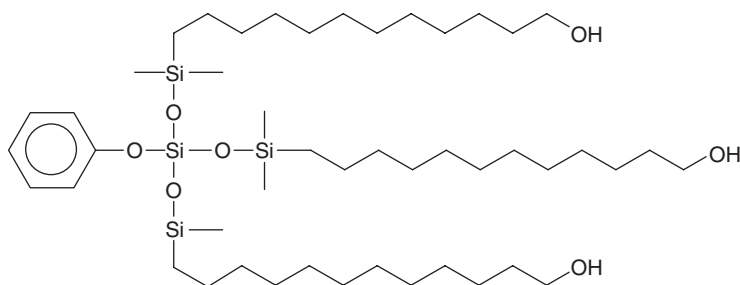

Scheme 3.8
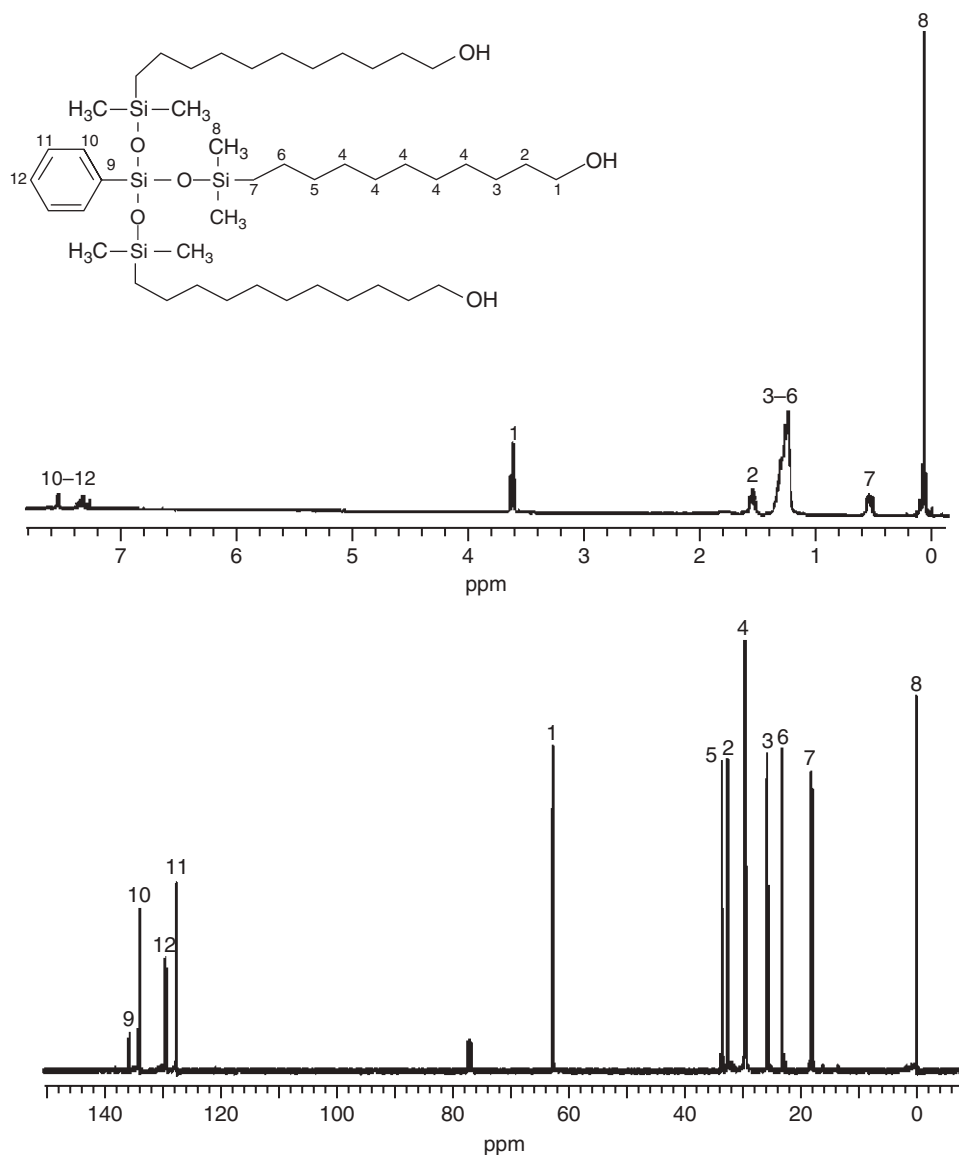
Figure 3.9 NMR spectra of the Si-oil-polyol reported in Reference [69]. (Reproduced by permission of the American Chemical Society, Copyright 2006. Reprinted from Reference [69]).

of their thixotropic character [70]. The best known polyamide in this context, Nylon 11, is now 30-years old and although this polymer has good properties like dimensional stability, chemical resistance and low cold brittleness temperature, research in this field has not been pursued [71, 72].

3.4.9 Oil-based polyester-amides

Polyester-amides, as such, or filled with alumina particles, were prepared from N,N′-bis(2 hydroxyethyl) **LO** (**HELA**) and phthalic acid, in the presence or absence of poly(styrene-co-maleic anhydride), with the aim of preparing novel surface coating materials [73–75]. These polymers were further modified with **TDI**, in order to
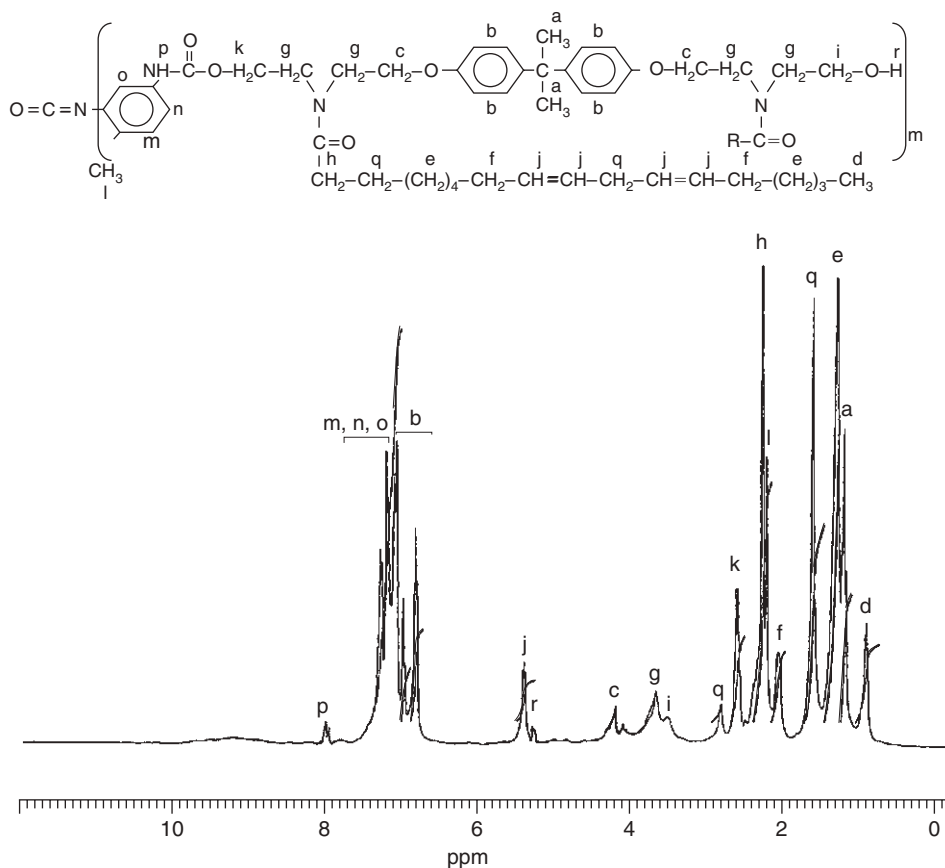
Figure 3.10 ^{1}H-NMR spectrum of PEA–TDI polyester-amide-urethane reported in Reference [76]. (Reproduced by permission of Elsevier. Copyright 2004. Reprinted from Reference [76]).

improve their adhesion, toughness and water and chemical resistances [76]. Figure 3.10 shows the NMR spectrum of these modified materials.

Other oils, specific to India like *Pongamia glabra* and Nahar (*Mesua ferrea*), as well as boron-based **SOYO,** have also been used in the preparation of polyester-amides [77–79]. These materials were used for coating at curing temperatures of 185°C–250°C. The toxicity evaluation and skin irritation tests showed that these polyester-amides were biologically safe for industrial applications. These materials also showed improved gloss, hardness adhesion and chemical resistance [77, 78]. The boron-based homologues were found to be good candidates for biomedical applications, because they exhibited anti-microbial properties [79].

3.4.10 Oil-based alkyd resins and polyesters

Alkyd resins can be prepared from either monoglycerides or fatty acids. The former approach is based on the alcoholysis of the oil by part of a polyol, followed by the esterification of the remaining hydroxy functions using a polyacid. The latter approach is instead based on a one-step process consisting of the direct reaction among the fatty acid, the polyol and a polyacid [14].

Traditionally, **SFO**, **SOYO**, **LO** and rapeseed oils have been used in the preparation of oil-modified polyesters, mainly in the field of offset printing inks, but new vegetable oils, such as rubber seed, karinatta, orange seed and melon seed oils were recently employed for this purpose [80]. Different anhydrides have been used to prepare alkyd resins, namely: maleic (**MAA**), succinic (**SA**), glutaric (**GA**), and phthalic (**PA**) [81]. Generally, in coating and printing, the drying time is one of the most relevant parameters. Resins prepared with **MAA** showed the best water resistance properties and the shortest drying time when **SFO** was used as the oil base.
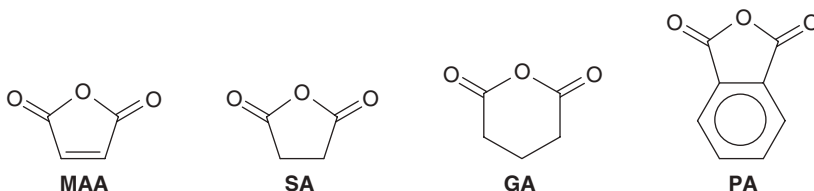
Liquid crystals from alkyd resins were reported 20 years ago [82, 83]. They were investigated with the aim of using them as coatings because they could be processed without a solvent and gave improved film properties. These materials were prepared by reacting *p*-hydroxybenzoic acid (**PHBA**) with hydroxy- or carboxy-terminated, or **SA**-modified alkydresins, as shown in Scheme 3.9.

Ecology-friendly water-based organic coatings have attracted much attention because of the absence of volatile organic compounds. For this purpose, ammonium salts of alkyd resins with high acid numbers have been used successfully [84–86]. Nakayama [87] prepared oil-based resin blends for water-borne paints by copolymerizing **ST**, **MMA** or **AA** with unsaturated fatty acid esterified glycidyl methacrylate. One of the resins reported in this study was an **ST**-allylalcohol copolymer, which was first esterified with **LO** fatty acids and then maleinized [87].

Recently reported highly branched oil-based alkyd resins were shown to be particularly interesting because their reduced viscosity allowed high solid contents coatings to be prepared [88].

Rubber seed oils (**RSO**) have also been used to prepare alkyd emulsions after their modification with **MAA** and **PA**, which produced water-soluble alkyd materials [86].

In another approach, **RSO**-based polyesters were prepared as shown in Scheme 3.10 and showed good chemical resistance [89]. Similar work based on the hydrosilylation of fatty acids and the preparation of hybrid organic–inorganic materials has also been reported [90].
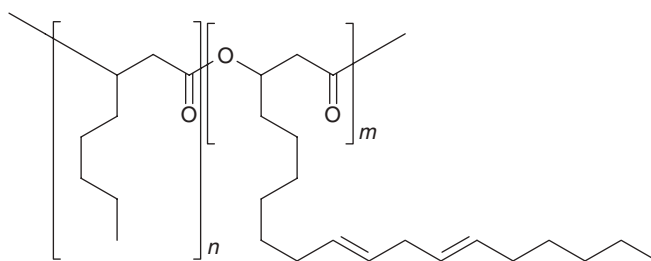
Scheme 3.9
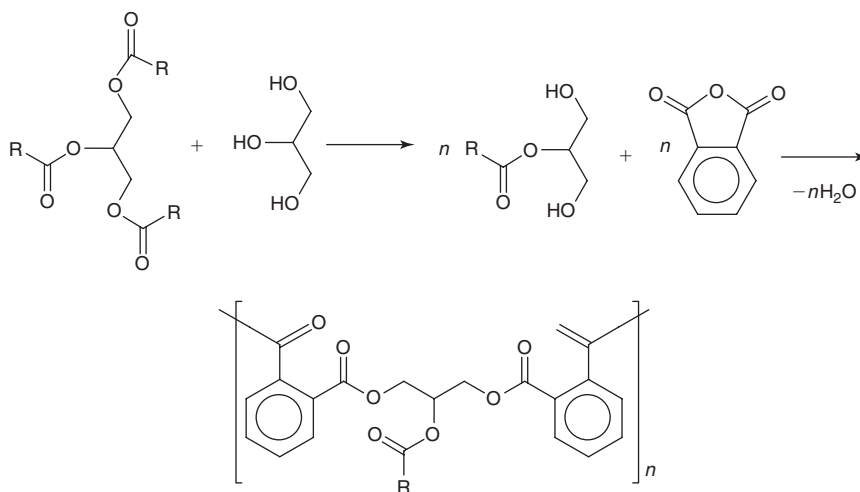
Scheme 3.10

A series of monooleate-polyethylene glycols with active carboxy functions arising from the condensation of succinic anhydride has been recently reported [91]. Their molecular weights, determined by GPC, varied from 760 to 10,340, depending on the reaction conditions and the monomers' stoichiometry. Partially bio-based unsaturated polyesters, containing epoxidized methyl linseedate, were prepared and showed that up to 25 per cent w/w of linseedate could be included into these formulations [92]. The incorporation of this vegetable oil derivative improved the thermal and mechanical properties of the ensuing polyesters.

3.4.11   Oil-based poly(hydroxyalcanoates)

Polyhydroxyalkanoates (PHAs) have attracted much attention because of their renewable character and good properties [93], as discussed in detail in Chapter 22. Vegetable oils are among the different feeding sources for the bacteria and only some features specific to this issue will be discussed in this chapter. Tallow oil has been used to prepare a semi-crystalline medium chain-length PHA, using the *Pseudomonas resinovorans* bacterium, with a Tg of $-43°C$ and a melting temperature of $43°C$ [94]. The presence of insaturations within the side chains produced crosslinked materials when this PHA was irradiated with γ-rays. The radiation doses were found to increase the tensile properties of the films, but reduce their rate of biodegradation. Blends of tallow- and **LO**-based PHAs were also prepared and characterized [94]. Two years later, the same group prepared medium chain-length **LO**-based PHA (**PHA–L**), as a viscous liquid polymer [95]. The side chain insaturations were then converted into epoxy moieties (**PHA–LE**), using *m*-chloroperoxibenzoic acid, as shown in Scheme 3.11. Figure 3.11 shows the ^{13}C-NMR spectra of the **PHA–L** before and after epoxidation. As expected, the epoxidation increased the crosslinking rate and the tensile strengths of the corresponding networks.

The preparation of medium chain-length PHA using **LO** and *Pseudomonas putida* has also been reported [96]. These resins displayed a high ability to undergo oxidative drying (high amount of insaturations within the fatty acid side chains) and the ensuing paints had excellent coating properties with good adhesion to different substrates [96].

3.4.12   Miscellaneous

A wide variety of polymeric materials, other than those discussed previously, are described in the literature. Given once again the availability of recent monographs [1–5], we will limit our treatment of this rather marginal system, to some relevant examples. Polynaphthols were synthesized by combining artificial urushi and triglyceride [97, 98] and, in another vein, acrylic diene metathesis polymerization was applied to triglyceride [99–101]. Composites with oil-based matrices have been frequently described [4] and continue to arise interest as shown by recent contributions [102–104].
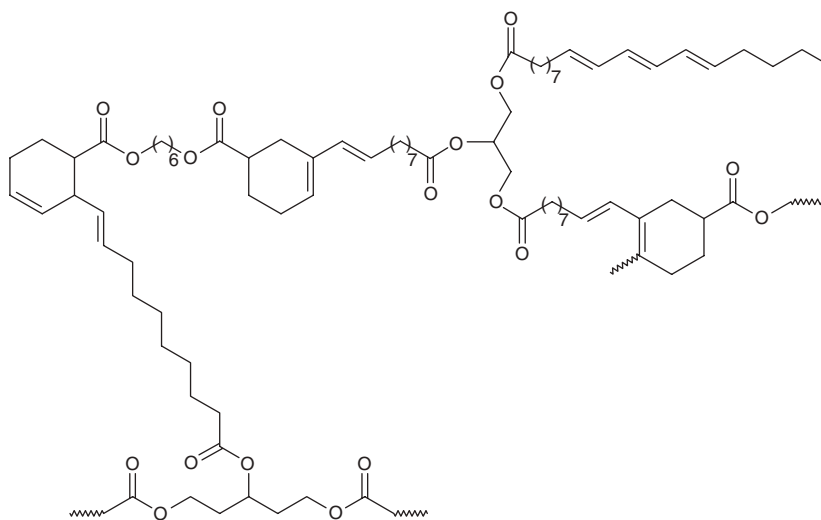

PHA–L   **PHA–LE**
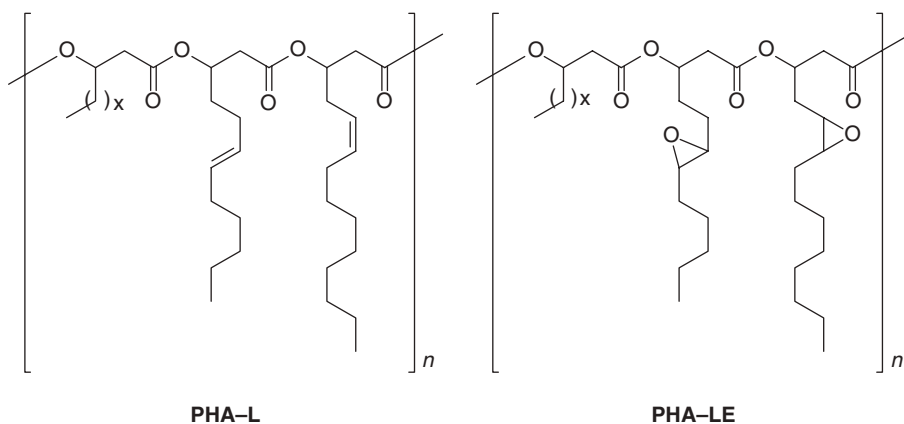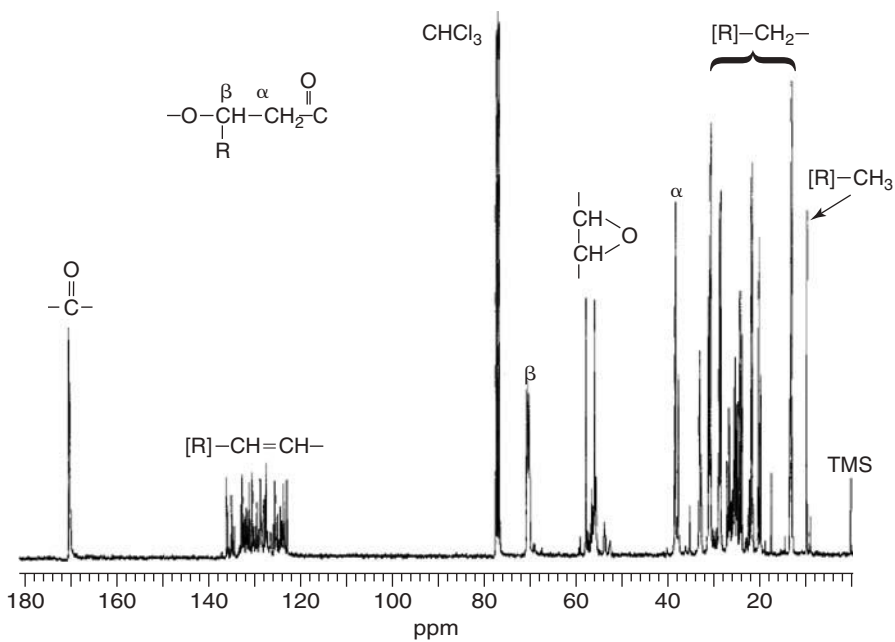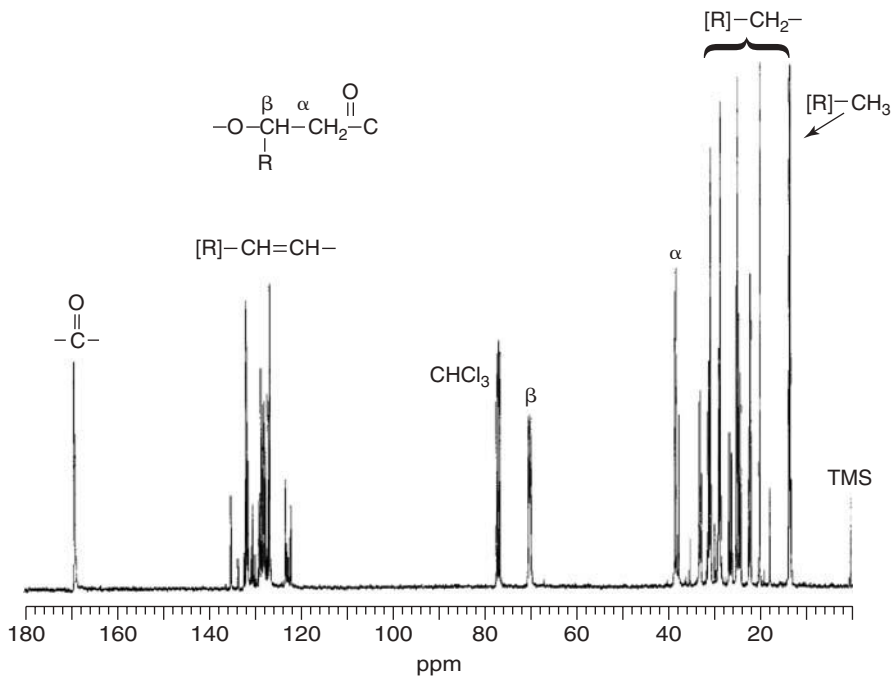
Scheme 3.11

Figure 3.11 ^{13}C-NMR spectra of (a) **PHA–L** and (b) **PHA-LE**. (Reproduced by permission of Elsevier. Copyright 2000. Reprinted from Reference [95]).
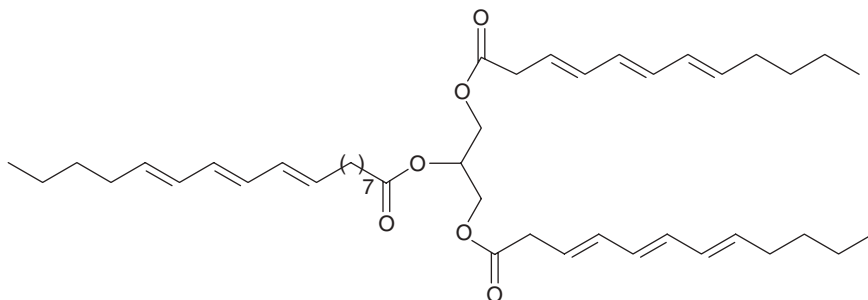
Scheme 3.12

Scheme 3.13

Trumbo and Mote prepared crosslinked networks from **TO** (Scheme 3.12), *via* a Diels–Alder reaction [105], using 1,6-hexanediol- and 1,4-butanediol-diacrylates. They characterized their product and showed that some combinations gave films with 95 per cent of gel fraction. Scheme 3.13 shows the idealized network structure proposed by these authors. The corresponding films had high gloss and good solvent resistance.

Buriti oil (**BO**) was mixed with **PST** or **PMMA** and the ensuing blends characterized in terms of absorption and photoluminescence properties associated with the specific structure of this oil extracted from an Amazonian palm tree [106]. Liu *et al.* reported very recently that **SOYO** can be homo-polymerized in CO_2 supercritical conditions by cationic initiation with **BFE** without using a co-monomer [107].

Electrically conductive polyurethane membranes based on **CO** and doped with sulfonated polyaniline were prepared and characterized [108]. Their Tgs varied from -8 to 28°C, depending on the NCO/OH ratio.

SOYO's fatty acid was transformed into the corresponding terminal oxazoline derivative, which was then polymerized using a microwave assisted technology (Scheme 3.14) [109]. This polymer was found to crosslink when irradiated by UV light, because of the insaturations borne by the **SOYO** alkyl chains [109].

The inclusion of carbon black into polymers based on **ASOYO** was shown to display interesting modulated electrical resistivity, as a function of the filler content [110]. A percolation threshold was attained with only 1.2 per cent of carbon black and an associated resistivity of about $10^{11}\,\Omega\,cm$.

A recent original approach to the use of vegetable oils as precursors to polyurethanes describes the ozone-induced oxidation of the single insaturations borne by each chain of canola oil triglyceride followed by the cleavage and hydroxylation of the ensuing end groups (Scheme 3.15) [110]. This triol macromonomer was then mixed

Scheme 3.14

Ozonolysis

Zinc

H₂, Ni catalyst
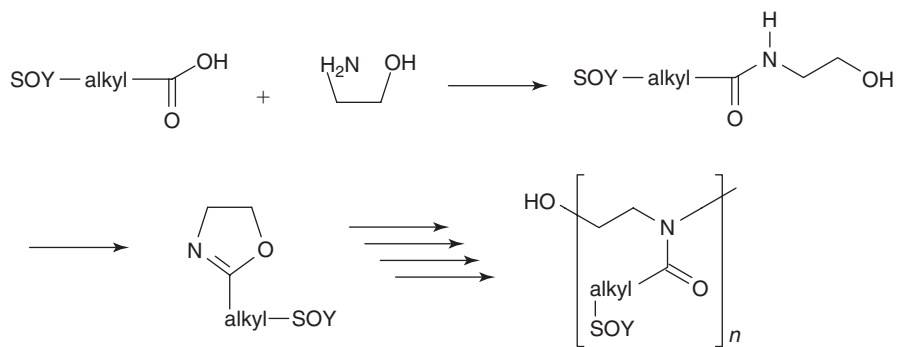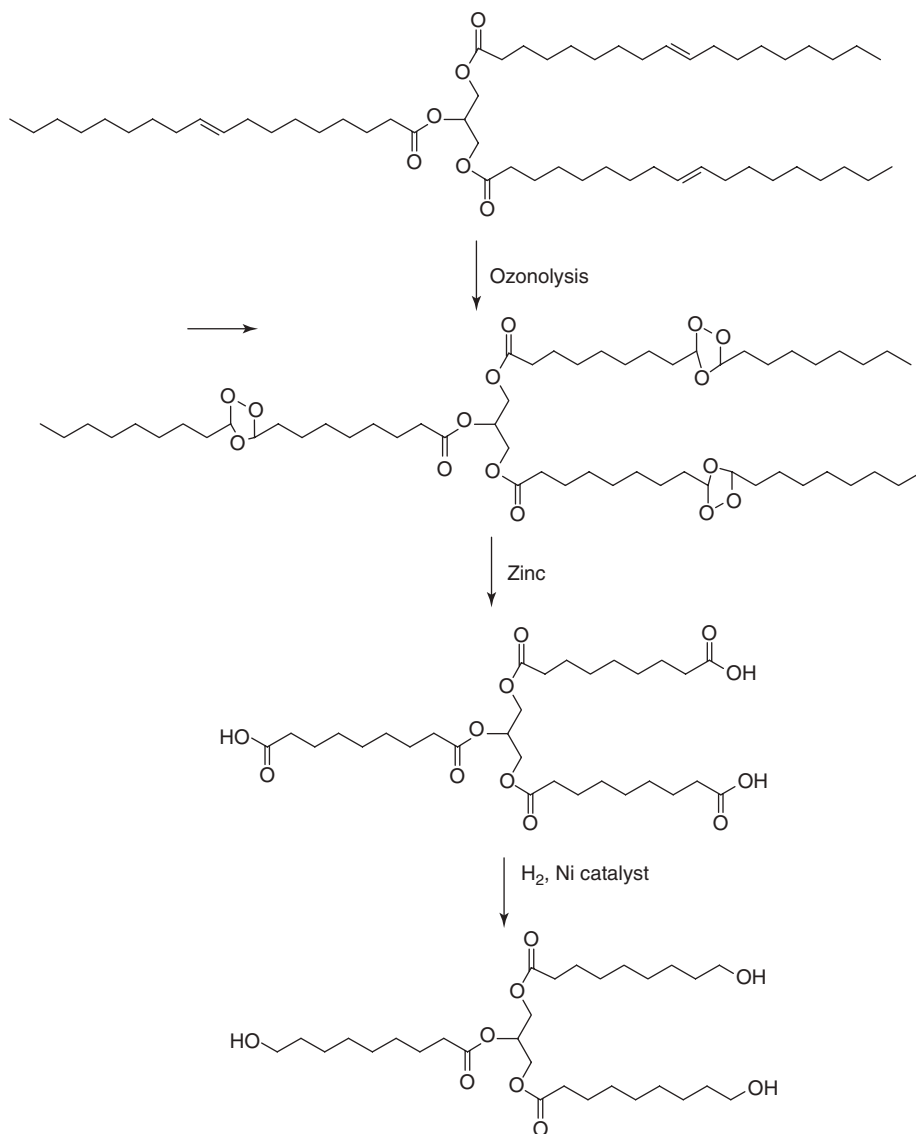
Scheme 3.15

with **MDI** to prepare the corresponding polyurethanes which were thoroughly characterized. However, given the rather tortuous pathway leading to the triol and the fact that a half of the aliphatic carbon chain is lost in this process, the actual economic feasibility of this approach is doubtful.

3.5   CONCLUSIONS

The aim of this chapter was to highlight the potentiality of triglyceride oils in the field of the synthesis of polymeric materials from renewable resources and the main messages we tried to deliver are that:

 (i)   the presence of oil or oil derivatives (fatty acid chains) in different formulations for coating or printing improves the optical (gloss), physical (flexibility, adhesion) and chemical properties (resistances to water and chemicals) of the cured films;

 (ii)   in some instances, soybean oil-based polymeric materials have properties comparable with those of petroleum-based counterparts;

 (iii)   the modification of these oils can lead to macromonomers susceptible to polymerize via very fast light-induced mechanisms, a fact that again compares favourably with the behaviour of equivalent acrylic formulations.

   The almost simultaneous publication of reviews and monographs on the topic covered by this chapter, together with the increasing flow of more specific studies covering a wide range of oils and related chemical modifications, represent indisputable proof about the relevance of this realm.

REFERENCES

 1. Verhé R.G., Industrial products from lipids and proteins, in *Renewable Bioresources: Scope and Modification for Non-Food Applications* (Eds. Stevens C.V. and Verhé R.G.), John Wiley & Sons, Ltd, Chichester, 2004, pp. 208–250, Chapter 9.
 2. Güner F.S., Yagci Y., Erciyes A.T., *Prog. Polym. Sci.*, **31**, 2006, 633.
 3. Sharma V., Kundu P.P., *Prog. Polym. Sci.*, **31**, 2006, 983.
 4. Wool R.P., Sun X.S., *Bio-Based Polymers and Composites*, Elsevier, Amesterdam, 2005.
 5. Gunstone F., *Fatty acid and lipid chemistry*, Blackie Academic & Professional, New York, 1996.
 6. Cunningham A., Yapp A., US Patent, 3,827,993, 1974.
 7. Bussell G.W., US Patent, 3,855,163, 1974.
 8. Hodakowski L.E., Osborn C.L., Harris E.B., US Patent, 4,119,640, 1975.
 9. Trecker D.J., Borden G.W., Smith O.W., US Patent, 3,979,270, 1976.
10. Trecker D.J., Borden G.W., Smith O.W., US Patent, 3,931,075, 1976.
11. Salunkhe D.K., Chavan J.K., Adsule R.N., Kadam S.S., *World Oilseeds: Chemistry, Technology and Utilization*, Van Nostrand Reinhold, New York, 1992.
12. Force C.G., Starr F.S., US Patent, 4,740,367, 1988.
13. Khot S.N., Lascala J.J., Can E., Morye S.S., Williams G.I., Palmese G.R., Kusefoglu S.H., Wool R.P., *J. Appl. Polym. Sci.*, **82**, 2001, 703.
14. Deligny P.K.T., Tuck N., Alkyds and polyeste*rs*, in *Resins for Surface Coatings* (Ed. Oldring P.K.T.), Wiley, New York, 2000, Volume II.
15. Bailey A.E., *Bailey's Industrial Oil and Fat Products*, Wiley, New York, 1996.
16. Norris F.A., Extraction of fats and oils, in *Bailey' s Industrial Oil and Fat Products* (Ed. Swern D.), Wiley, New York, 1996, Volume II.
17. Johnson R.W., Fritz E E., *Fatty Acids in Industry*, Marcel Dekker, New York, 1989.
18. Li F., Larock R.C., Otaigbe J.U., *Polymer*, **41**, 2000, 4849.
19. Li F., Larock R.C., Marks D.W., Otaigbe J.U., *Polymer*, **41**, 2000, 7925.
20. Li F., Larock R.C., *J. Appl. Polym. Sci.*, **78**, 2000, 1044.
21. Li F., Larock R.C., *J. Appl. Polym. Sci.*, **78**, 2000, 2721.
22. Li F., Larock R.C., *J. Appl. Polym. Sci.*, **80**, 2001, 658.
23. Li F., Hanson M.V., Larock R.C., *Polymer*, **42**, 2001, 1567.
24. Li F., Perrenoud A., Larock R.C., *Polymer*, **42**, 2001, 10133.

25. Li F., Larock R.C., *J Polym Sci B: Polym Phys*, **39**, 2001, 60.
26. Marks D.W., Li F., Pacha C.M., Larock R.C., *J. Appl. Polym. Sci.*, **81**, 2001, 2001.
27. Li F., Larock R.C., *J. Appl. Polym. Sci.*, **84**, 2002, 1533.
28. Li F., Larock R.C., *Polym. Int.*, **52**, 2003, 126.
29. Li F., Hasjim J., Larock R.C., *J. Appl. Polym. Sci.*, **90**, 2003, 1830.
30. Li F., Larock R.C., *Biomacromolecules*, **4**, 2003, 1018.
31. Kundu P.P., Larock R.C., *Biomacromolecules*, **4**, 2005, 797.
32. Andjelkovic D.D., Larock R.C., *Biomacromolecules*, **4**, 2006, 927.
33. Lu Y., Larock R.C., *Biomacromolecules*, **7**, 2006, 2692.
34. Henna P.H., Andjelkovic D.D., Kundu P.P., Larock R.C., *J. Appl. Polym. Sci.*, **104**, 2007, 979.
35. Gultekin M., Beker U., Güner F.S., Erciyes A.T., Yagsi Y., *Macromol. Mater. Eng.*, **283**, 2000, 15.
36. Hazer B., Demirel S.I., Borcakli M., Eroglu M.S., Cakmak M., Erman B., *Polym. Bull.*, **46**, 2001, 389.
37. Akbas T., Beker U.G., Güner F.S., Erciyes A.T., Yagsi Y., *J. Appl. Polym. Sci.*, **88**, 2003, 2373.
38. Eren T., Küsefoglu S.H., *J. Appl. Polym. Sci.*, **97**, 2005, 2264.
39. Zong Z., He J., Soucek M.D., *Prog. Org. Coat.*, **53**, 2005, 83.
40. Can E., Wool R.P., Küsefoglu S., *J. Appl. Polym. Sci.*, **102**, 2006, 2433.
41. Can E., Wool R.P., Küsefoglu S., *J. Appl. Polym. Sci.*, **102**, 2006, 1497.
42. Tuman S.J., Chamberlain D., Scholsky K.M., Soucek M.C., *Prog. Org. Coat.*, **28**, 1996, 251.
43. Meneghetti S.M.P., de Souza R.F., Monteiro A.L., de Souza M.O., *Prog. Org. Coat.*, **33**, 1998, 219.
44. Turri B., Vinci S., Margutti S., Pedemonte E., *J. Therm. Anal. Calor.*, **66**, 2001, 343.
45. Fried R.J., *Polymer Science and Technology*, 2nd Edition, Pearson Education, New Jersey, 2003.
46. Sperling L.H., Manson J.A., Yenwo G.M., Devia-Manjarres N., Pulido J., Conde A., *Polym. Sci. Technol.*, **10**, 1977, 113.
47. Nayak P.L., *J. Macromol. Sci. Rev. Macromol. Chem. Phys.*, **40**, 2000, 1.
48. Yin Y., Yao S., Zhou X., *J. Appl. Polym. Sci.*, **88**, 2003, 1840.
49. Crivello J.V., Narayan R., *Chem. Mater.*, **4**, 1992, 692.
50. Crivello J.V., Carlson K.D., *Macromol. Reports*, **A33**(suppl 5 and 6), 1996, 251.
51. Crivello J.V., Narayan R., Sternstein S.S., *J. Appl. Polym. Sci.*, **64**, 1997, 2073.
52. Ortiz R.A., Lopez D.P., de L. Guillen Cosneros M., Valverde J.C.R., Crivello J.V., *Polymer*, **46**, 2005, 1535.
53. Boquillon N., Fringant C., *Polymer*, **41**, 2000, 8603.
54. Eren T., Küsefoglu S.H., *J. Appl. Polym. Sci.*, **91**, 2004, 2700.
55. Shukla V., Singh M., Singh D.K., Shukla R.I., *Surf. Coat. Int. Part B: Coat. Trans.*, **88**(B3), 2005, 157–230. 157
56. Ashraf S.M., Ahmad S., Riaz U., Alam M., Sharma H.O., *J. Macromol. Sci., Part A: Pure Appl. Chem*, **42**, 2005, 1409.
57. Ashraf S.M., Ahmad S., Riaz U., Sharma H.O., *J. Appl. Polym. Sci.*, **100**, 2006, 3094.
58. Zou K., Soucek M.D., *Macromol. Chem. Phys.*, **206**, 2005, 967.
59. Park S.J., Jin F.L., Lee J.R., Shin J.S., *Eur. Polym. J.*, **41**, 2005, 231.
60. H. Pelletier, Ph.D Thesis, Grenoble National Polytechnic Institute, 2005.
61. Pelletier H., Gandini A., *Eur. J. Lipid Sci. Technol.*, **108**, 2006, 411.
62. Pelletier H., Belgacem M.N., Gandini A., *J. Appl. Polym. Sci.*, **99**, 2006, 3218.
63. Earls J.D., White J.E., Lopez L., Lysenko Z., Dettloff M.L., Null M.J., *Polymer*, **48**, 2007, 712.
64. Esen H., Küsefoglu S.H., Wool R., *J. Appl. Polym. Sci.*, **103**, 2007, 626.
65. Guner F.S., Baranak M., Soytas S., Erciyes A.T., *Prog. Org. Coat*, **50**, 2004, 172.
66. Yeganeh H., Mehdizadeh M.R., *Eur. Polym. J.*, **40**, 2004, 1233.
67. Ozkaynak M.U., Atalay-Oral C., Tantekin-Ersolmaz S.B., Guner F.S., *Macromol. Symp.*, **228**, 2005, 177.
68. Gunduz G., Khalid A.H., Mecidoglu A., Aras L., Waterborne and air-drying oil-based resins, *Prog. Org. Coat.*, **49**, 2004, 259.
69. Lligadas G., Ronda J.C., Galia M., Cadiz V., *Biomacromolecules*, **7**, 2006, 2420.
70. Oldring P.K.T., Turk N., *Polyamides. Resins for Surface Coatings*, Wiley, New York, 2000, Volume III, pp. 131–197.
71. Nayak P.L., Natural oil-based polymers: Opportunities and challenges, *J. Macromol. Sci. Rev. Macromol. Chem. Phys.*, **40**, 2000, 1.
72. Koch R., Nylon 11, *Polym. News*, **3**, 1977, 302.
73. Ahmad S., Naqvi F., Verma K.L., Yadav S., *J. Appl. Polym. Sci.*, **72**, 1999, 1679.
74. Ahmad S., Ashraf S.M., Hasnat A., Yadav S., Jamal A., *J. Appl. Polym. Sci.*, **82**, 2001, 1855.
75. Zafar F., Ashraf S.M., Ahmad S., *Prog. Org. Coat.*, **50**, 2004, 250.
76. Alam M., Sharmin E., Ashraf S.M., Ahmad S., *Prog. Org. Coat.*, **50**, 2004, 224.
77. Ahmad S., Ashraf S.M., Naqvi F., Yadav S., Hasnat A., *Prog. Org. Coat.*, **47**, 2003, 95.
78. Mahapatra S.S., Karak N., *Prog. Org. Coat.*, **51**, 2004, 103.
79. Ahmad S., Haque M.M., Ashraf S.M., Ahmad S., *Eur. Polym. J.*, **40**, 2004, 2097.
80. Igwe I.O., Ogbobe O., *J. Appl. Polym. Sci.*, **75**, 2000, 1441.

81. Aydin S., Akçay H., Ozkan E., Guner F.S., Erciyes A.T., *Prog. Org. Coat.*, **51**, 2004, 273.
82. Chiang W.Y., Yan C.S., *J. Appl. Polym. Sci.*, **46**, 1992, 1279.
83. Chen D.S., Jones F.N., *J. Coat. Technol.*, **60**(756), 1988, 39.
84. Hofland A., *Surf. Coat. Int.*, **7**, 1994, 270.
85. Rødsrud G., Sutcliffe J.E., *Surf. Coat. Int.*, **1**, 1994, 7.
86. Aigbodion A.I., Okieimen F.E., Obazee E.O., Bakare I.O., *Prog. Org. Coat.*, **46**, 2003, 28.
87. Nakayama Y., *Prog. Org. Coat.*, **33**, 1988, 108.
88. Manczyk K., Szewzzyk P., *Prog. Org. Coat.*, **44**, 2002, 99.
89. Bakare I.O., Pavithran C., Okieimen F.E., Pillai C.K.S., *J. Appl. Polym. Sci.*, **100**, 2006, 3748.
90. Lliagadas G., Callau L., Ronda J.C., Cadiz V., *J. Polym. Sci., Part A: Polym. Chem.*, **43**, 2005, 6295.
91. Xiong F., Li J., Wang H., Chen Y., Cheng J., Zhu J., *Polymer*, **47**, 2006, 6636.
92. Miyagawa H., Mohanty A.K., Burgueno R., Drzal L.T., Misra M., *Ind. Eng. Chem. Res.*, **45**, 2006, 1014.
93. Braunegg G., Lefebvre G., Genser K.F., *J. Biotechnol.*, **65**, 1988, 127.
94. Ashby R.D., Cromwick A., Foglia T.A., *Int. J. Biol. Macromol.*, **23**, 1998, 61.
95. Ashby R.D., Foglia T.A., Solaiman D.K.Y., Liu C., Nunez A., Eggink G., *Int. J. Biol. Macromol.*, **27**, 2000, 355.
96. van der Walle G.A.M., Buisman G.J.H., Weusthuis R.A., Eggink G., *Int. J. Biol. Macromol.*, **25**, 1999, 123.
97. Kobayashi S., Uyama H., Ikeda R., Artificial urushi, *Chem. Eur. J.*, **7**, 2001, 4754.
98. Tsujimoto T., Uyama H., Kobayashi S., *Macromolecules*, **37**, 2004, 1777.
99. Tian Q., Larock R.C., *J. Am. Oil. Chem. Soc.*, **79**, 2002, 479.
100. Warwel S., Bruse F., Demes C., Kunz M., gen Klaas M.R., *Chemosphere*, **43**, 2001, 39.
101. Warwel S., Bruse F., Demes C., Kunz M., *Ind. Crops Prod.*, **20**, 2004, 301.
102. O'Donnell A., Dweib M.A., Wool R.P., *Comp. Sci. Technol.*, **64**, 2004, 1135.
103. Wang Y., Cao X., Zhang L., *Macromol. Biosci.*, **6**, 2006, 524.
104. Chen Y., Zhang L., Deng R., Liang H., *J. Appl. Polym. Sci.*, **101**, 2006, 953.
105. Trumbo D.L., Mote B.E., *J. Appl. Polym. Sci.*, **80**, 2001, 2369.
106. Duraes J.A., Drummont A.L., Piemental T.A.P.F., Murta M.M., Bicalho F., da S., Moreira S.G.C., Sales M.J.A., *Eur. Polym. J.*, **42**, 2006, 3324.
107. Liu Z., Sharma B.K., Erhan S.Z., *Biomacromolecules*, **8**, 2007, 233.
108. Amado F.D.R., Rodrigues L.F., Forte M.M.C., Ferreira C.A., *Polym. Eng. Sci.*, **46**, 2006, 1485.
109. Hoogenboom R., Schubert U.S., *Green Chem.*, **8**, 2006, 895.
110. Hernandez-Lopez S., Vegueras-Santiago E., Mercado-Posadas J., Snachez-Mendieta V., *Adv. Tech. Mater. Mater. Proc. J.*, **8**, 2006, 214.
111. Kong X., Narine S.S., *Biomacromolecules*, **8**, 2007, 2203.

– 4 –

Rosin: Major Sources, Properties and Applications

Armando J.D. Silvestre and Alessandro Gandini

ABSTRACT

Rosin exploitation, a part of the so-called Naval Stores Industry, is at least as old as the construction of wooden naval vessels. In recent years, rosin components have attracted a renewed attention, notably as sources of monomers for polymers synthesis. The purpose of the present chapter is to provide a general overview of the major sources and composition of rosin. It deals therefore with essential features such as the structure and chemical reactivity of its most important components, viz. the resin acids, and the synthesis of a variety of their derivatives. This chemical approach is then followed by a detailed discussion of the relevant applications, the resin acids and their derivatives, namely in polymer synthesis and processing, paper sizing, emulsion polymerization, adhesive tack and printing inks, among others.

4.1   INTRODUCTION

Rosin exploitation, a part of the so-called Naval Stores Industry, is at least as old as the construction of wooden naval vessels. It was however only during the first half of the twentieth century that the chemistry of this natural resource was studied in detail and new transformations and applications developed on a more scientific basis. A vast number of papers and patents are available on these topics and most of the relevant information were comprehensively reviewed in the classical book edited by Zinkel and Russell in 1989 [1], which covered all aspects, from the sources and processing, to the chemistry and applications of this versatile raw material. A less exhaustive survey, devoted to rosin applications for polymer synthesis, was also published in the same year by Maiti *et al.* [2].

Although the overall exploitation of rosin and its derivatives has been declining over the past few decades, it is the predicted depletion of fossil resources that is driving both the scientific community and industry to look for alternative renewable resources for the production of chemical commodities. It seems therefore logical that these abundant and cheap resins should witness an important comeback.

The purpose of the present chapter is to provide a general overview of the major sources, properties and both traditional and novel applications of rosin components, with particular emphasis on the most relevant contributions of the last couple of decades dealing with rosin as a source of monomers or additives for polymeric materials. A detailed analysis of the extensive bibliography on the various chemical transformations, as well as on other applications of rosin, falls outside the scope of this chapter, given the aim of this book.

Rosin, also known as colophony, is the common designation given to the non-volatile residue, mainly composed of resin acids, obtained after the distillation of the resin exuded by many conifer trees as a faintly aromatic,

semi-transparent brittle solid. The most important source of rosin is pine trees (*Pinus* genus), not only because they are widespread in the Northern Hemisphere, but also because of their intensive use in the timber and pulp industries.

For historical reasons, pine resin was known as "Naval Stores", because of its use in the waterproofing of wooden ships. Depending on the way pine resin is isolated from wood, three products are distinguished, namely (i) *gum naval stores*, obtained by tapping living trees; (ii) *sulphate naval stores*, also known as tall oil rosin, recovered during the kraft pulping of pine wood and (iii) *wood naval stores*, also known as wood rosin, obtained from the solvent extraction of harvested wood.

The total world rosin production tended to decline between the 1960s and the 1980s. However, statistics published in the 1980s [3] and in 1994 [4], show that the rosin production stabilized at around 1.0–1.2 million tons per year. According to the 1994 survey [4], gum rosin amounted to 60 per cent of world production, tall oil rosin to around 35 per cent and wood rosin to only a few percent.

The evolution of gum rosin production has been affected by two distinct factors, viz. the intense competition of petroleum-based counterparts and the growing costs of man-power involved in tree tapping and resin recovery. Competition from petroleum-based products was quite strong in the second half of the twentieth century, given the ready availability, low cost and technological development of petrochemicals. As already pointed out, this trend might be reversed in view of the increasing costs of fossil resources which will probably stimulate novel fundamental and applied research on the exploitation of rosin as a source of chemicals and materials. High man-power costs have contributed to the decline of gum rosin production in the industrialized North-American and European countries with the result of shifting it to other areas of the world such as China and Indonesia, which in the mid-1990s were already responsible for 60 and 10 per cent of world production, respectively. Whereas production in China is unlikely to grow any further because of limiting forestry factors, Indonesia still has a significant growth potential [4]. Brazil, Russia and Portugal were once also important producers, but they too are witnessing a significant drop in production [4].

4.2   ROSIN CHEMICAL COMPOSITION

Regardless of its origin (gum, wood or tall oil), rosin is mainly composed (90–95 per cent) of diterpenic mono-carboxylic acids, commonly known as resin acids whose generic formula is $C_{19}H_{29}COOH$. The remaining components are essentially made up of neutral compounds, the nature of which depends on the specific origin of the rosin [5]. The most common resin acids found in pine rosin are derived from the three basic tricyclic carbon skeletons abietane, pimarane and isopimarane and the less common bicyclic labdane skeleton (Fig. 4.1).

The abietane skeleton is shared by four resin acids (Fig. 4.2), namely abietic, neoabietic, palustric and levopimaric acids. The structures of these compounds, generally known as abietadienoic acids, differ only in the position of the conjugated double bond system, which is an important feature of this group of resin acids, because it
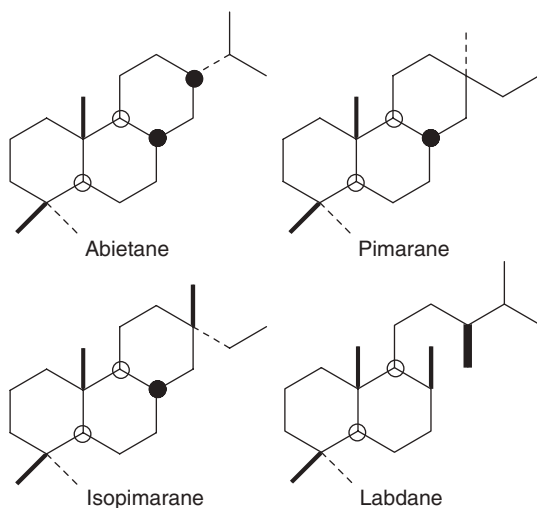
Figure 4.1   Diterpene carbon skeletons found in the most common resin acids.
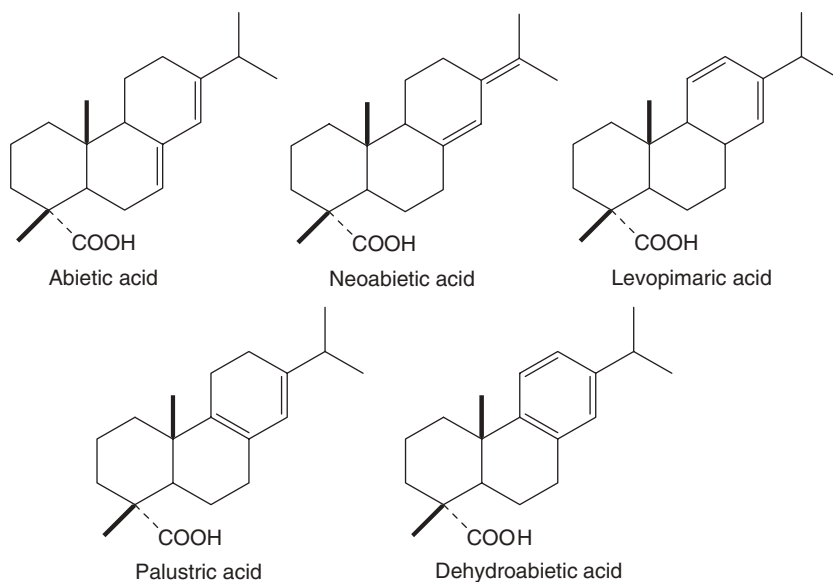
Figure 4.2   Structures of the most common abietane-type resin acids.
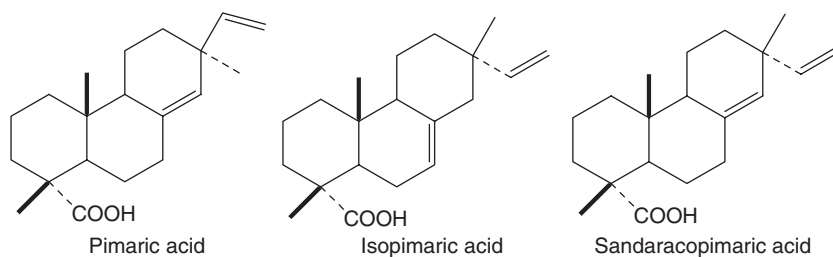
Figure 4.3   Structures of the most common pimarane-type resin acids.

influences their chemical reactivity and hence the applications of the ensuing products, as discussed below. The aromatic dehydroabietic acid is also found in small and variable amounts in various rosin species.

The most common pimarane-type acids are pimaric, isopimaric and sandaracopimaric acids (Fig. 4.3). Compared with the abietic counterparts, not only is the basic skeleton different but, more importantly, the double bond system is now not conjugated, a fact which reduces significantly the possible chemical exploitation of these compounds.

Although abietic-type acids are the dominant structures in most rosins, their relative abundance is quite variable, depending on the pine species and geographic origin. Furthermore, processing and handling conditions (*e.g.* temperature and pH) can induce the isomerization of the double bond system, leading to equilibrium mixtures, as discussed below.

From an industrial perspective, the quality of rosin and rosin derivatives is assessed on the basis of four basic parameters [4, 6], namely:

(1)   The *acid number*, which is a measure of the amount of free carboxylic groups; a decrease in this value is indicative of decarboxylation and/or functionalization of the carboxylic moieties.
(2)   The *saponification number*, which is a measure of the total amount of carboxylic groups; a decrease in this value is indicative of resin acid decarboxylation.
(3)   The *colour*, whose intensity is a key detrimental factor in many applications, is a measure of rosin oxidation; an increase in colour intensity is therefore an indication of decreasing quality.
(4)   The *softening point*, which is in fact a measure of the glass transition temperature associated with these complex mixtures of glassy materials; its value strongly influences the possible applications of these resins, as discussed below.

4.3 RESIN ACIDS CHEMICAL REACTIVITY

The chemical reactivity of resin acids is determined by the presence of both the double- bond system and the COOH group [5]. The carboxylic group is mainly involved in esterification, salt formation, decarboxylation, nitrile and anhydrides formation, etc. These reactions are obviously relevant to both abietic- and pimaric-type acids (Figs 4.1 and 4.3, respectively). The olefinic system can be involved in oxidation, reduction, hydrogenation and dehydrogenation reactions. Given the conjugated character of this system in the abietic-type acids, and the enhanced reactivity associated with it, much more attention has been devoted to these structures. In terms of industrial applications, salt formation, esterification, and Diels–Alder additions are the most relevant reactions of resin acids.

4.3.1 Reactions of the olefin system

The conjugated double bond system of abietadienoic acids is simultaneously a source of instability, detrimental for many rosin applications and, conversely, an interesting reactive centre for further modifications.

#### 4.3.1.1 Oxidation, hydrogenation and dehydrogenation

The conjugated double bond is responsible for rosin yellowing arising from oxygen addition, isomerization and other reactions. In many applications, this colouring is associated with a loss of product quality. Oxygen addition is normally photochemically induced, leading to the formation of epoxides, hydroxylated derivatives and endoperoxides [7] (Fig. 4.4). These unwanted reactions can be suppressed by dehydrogenation or hydrogenation processes.

Rosin dehydrogenation leads to the removal of hydrogen, which, after double bond rearrangement, converts abietadienoic acids into dehydroabietic acid [5, 8–11]. This reaction is normally carried out at high temperatures (200–300°C), often in the presence of catalysts like metals (*e.g.* Pd, Ni), sulphur or iodine. The hydrogen thus released reacts *in situ* by adding to the pimaradienoic acids and, to a smaller extent, to the abietadienoic acids. Both reactions contribute to the rosin stabilization and these products are known as disproportionated rosins.

If dehydrogenation is carried out at extreme temperatures and/or for long reaction times, the reaction proceeds more extensively and is accompanied by decarboxylation to form the neutral aromatic compound retene (Fig. 4.5) [5].
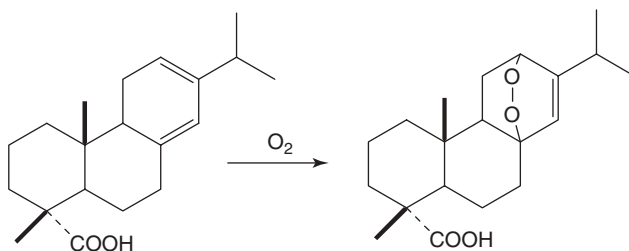
Figure 4.4 Oxidation of levopimaric acid with formation of an endoperoxide.
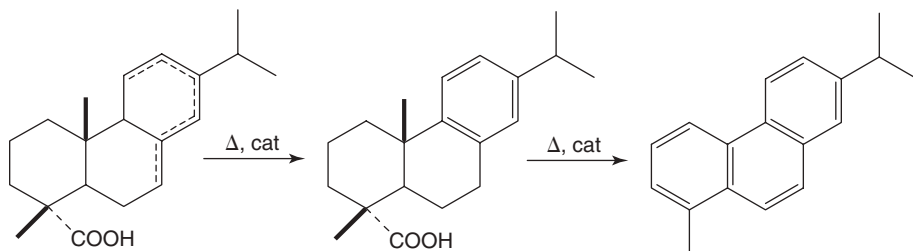
Figure 4.5 Conversion of abietadienoic acids into dehydroabietic acid and retene.
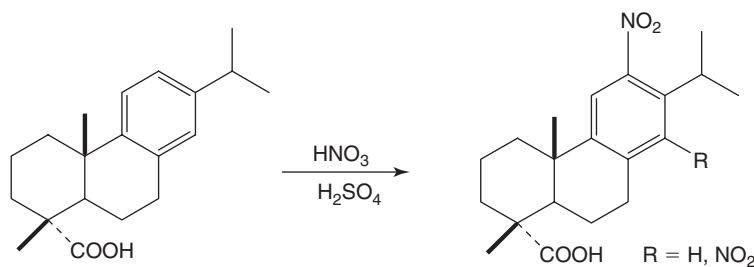
4.3.1.2 Functionalization of dehydroabietic acid aromatic ring

Dehydroabietic acid can undergo typical aromatic substitution reactions (*e.g.* acylation, chlorosulphonation, sulphonation and nitration) with preferential functionalization of the more reactive 12 position, followed in some cases by the 14 position. These reactions were first exploited in the 1930s–1940s [5, 12–14]. The nitration of dehydroabietic acid (Fig. 4.6) was one of the first reactions studied because of the synthetic versatility of the nitro group, namely as precursor of amino groups [14]. More recently, this reaction has been optimized using less harsh conditions [15, 16].

Hydrogenation is an efficient method for rosin stabilization. The reduction of the first (conjugated) double bond of abietadienoic acids with hydrogen in the presence of metal catalysts is relatively straightforward and frequently the ensuing dihydro-derivatives are stable enough for most applications. The reduction of the remaining double bond requires more severe conditions, but this process becomes necessary in the case of more stringent applications in terms of colour stability and oxygen resistance, such as with long-lifetime sealing agents, air-exposed varnishes, or even fresh-fruit film covering. These partially or fully hydrogenated rosins can then be used as precursors to other derivatives through the modification of the carboxylic functionality.

4.3.1.3 Isomerization

The chemical modifications of abietic-type acids through the conjugated double bond system must take into account a fundamental feature of these moieties, viz. their proneness to isomerization under heat and/or acidic conditions [17–22]. Thus, for example, abietadienoic acid mixtures undergo isomerization to give an equilibrium mixture of products in which abietic acid is the major component (~80 per cent), followed by palustric (~14 per cent) and neoabietic acids (~5 per cent), whereas levopimaric acid is only formed in trace amounts. Figure 4.7 shows the general mechanism of this isomerization process.

Figure 4.6   Nitration of dehydroabietic acid.
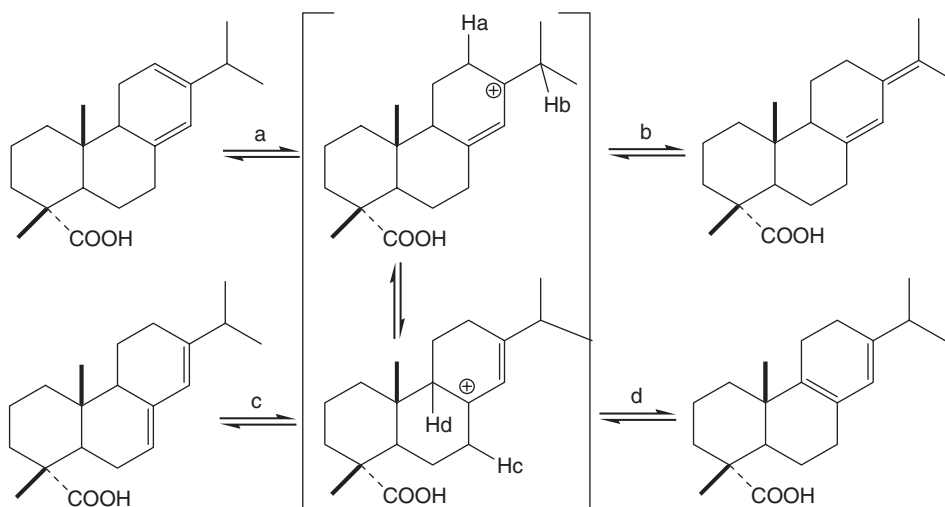
Figure 4.7   Mechanism of the acid-catalyzed isomerization of abietadienoic resin acids.
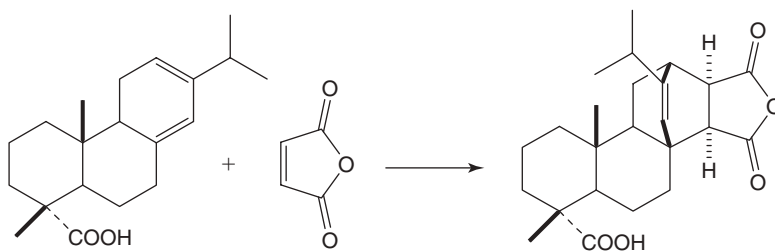
4.3.1.4   Diels–Alder reactions

When the Diels–Alder reaction with dienophiles is used to convert these acids into novel materials, its occurrence is optimized by the concomitant isomerization process giving levopimaric acid, which is the only homologue capable of producing an adduct. The equilibrium shown in Fig. 4.7 is then displaced by the consumption of levopimaric acid and the entire mixture is thus progressively consumed [5]. If, however, isomerization is minimized, this reaction can be used to isolate and quantify levopimaric acid [23]. Although the Diels–Alder reaction occurs essentially with levopimaric acid, it has been shown that in some instances it also takes place with palustric acid [24].

The Diels–Alder adduct between levopimaric acid and maleic anhydride, maleopimaric anhydride (Fig. 4.8) and the corresponding diacid are certainly the most important derivatives of this family mainly because of their applications in various domains. Levopimaric acid has also been used in the preparation of other adducts with a wide variety of dienophiles such as fumaric acid, acrylonitrile, acrylic acid, vinyl acetate and tetracyanoethylene [5].

The Diels–Alder reaction with maleic acid esters can be easily performed [25]. However, when it is carried out at high temperature ($\sim 250°C$), partial decarboxylation takes place, with formation of ketone-type dimers [26], yielding polyfunctional derivatives (Fig. 4.9) that could be good monomeric units for polymer synthesis [27].

The functionalities of several Diels–Alder adducts, or their derivatives, have been thoroughly exploited in the synthesis of polymeric materials, as discussed below.

**Figure 4.8**   Diels–Alder reaction of levopimaric acid with maleic anhydride.
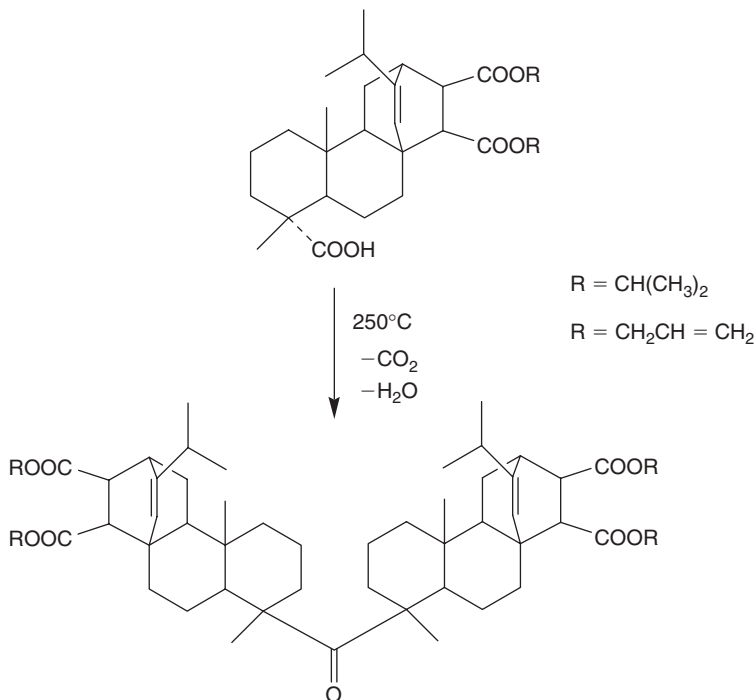
Figure 4.9   Formation of dimeric ketones of maleopimaric-type adducts [26].

4.3.1.5   Reactions with formaldehyde and phenol

Other relevant reactions of resin acids are those involving their addition to formaldehyde and/or phenols. Formaldehyde adds to abietic acid to form complex mixtures containing mono and dihydroxymethyl derivatives [28–31]. Under alkaline conditions, the formation of the mono derivative is favoured, whereas in acetic acid, the dihomologue (isolated as acetate) is the major product (Fig. 4.10). More recently, studies of the acid-catalyzed condensation of abietic acid with formaldehyde showed that, under such conditions the reactions mixtures were predominantly composed of trimeric structures [26, 32].

Since rosin can react with formaldehyde in a similar way as phenol, rosin components have also been used in the preparation of the corresponding rosin–phenol–formaldehyde resins with molecular weights and solubility that are adequate for their incorporation into printing inks. The incorporation of rosin components into phenol–formaldehyde prepolymers can occur through esterification or methylol condensation at one of the unsaturated carbons (Fig. 4.11).
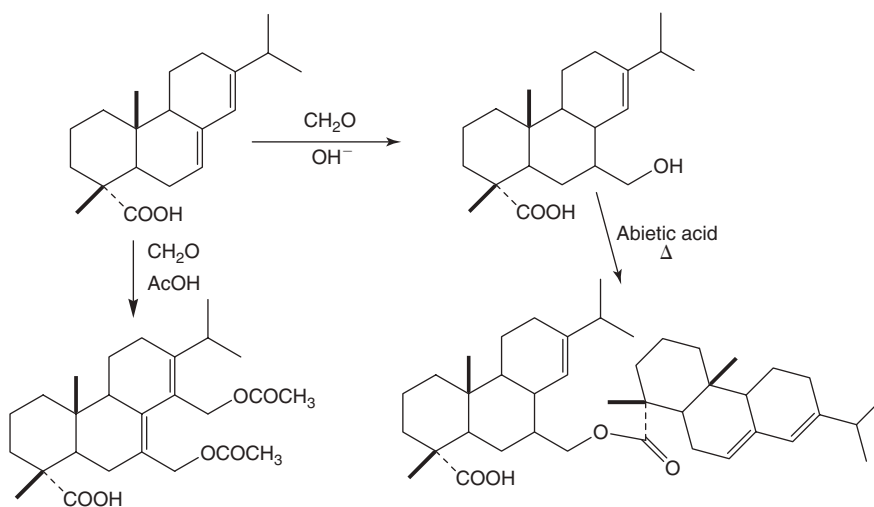
Figure 4.10   Addition of formaldehyde to abietic acid.
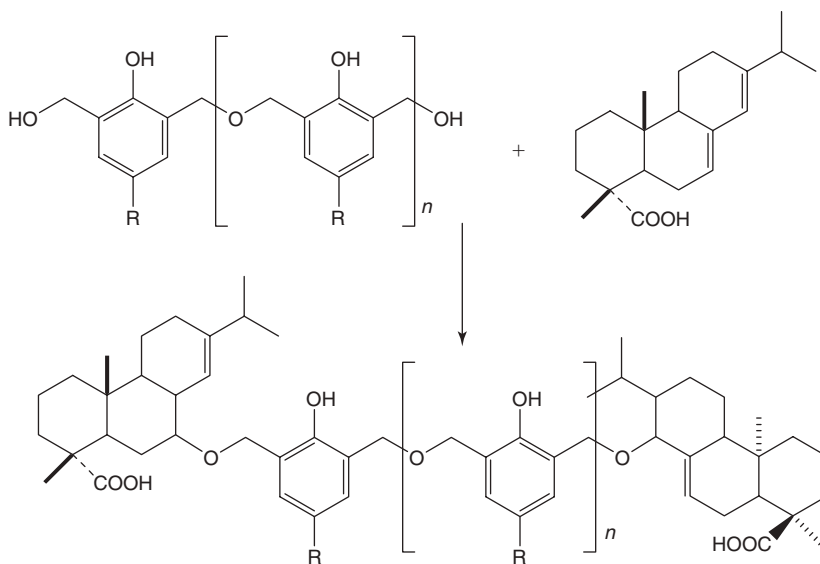
Figure 4.11   Formation of rosin-modified phenol–formaldehyde resins.
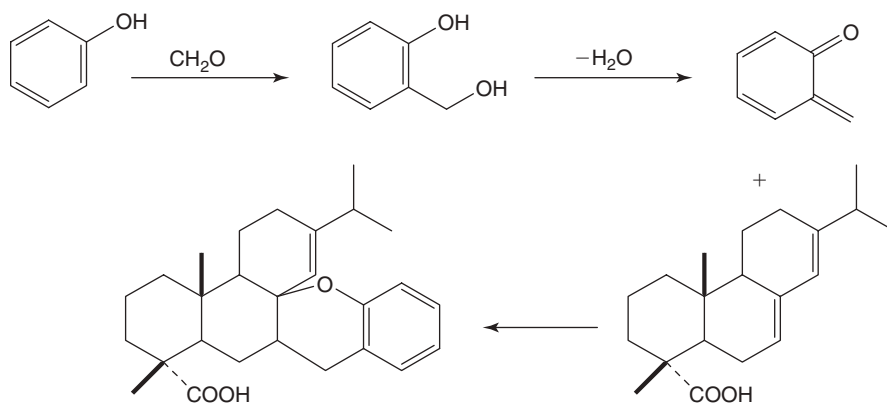
Figure 4.12   Formation of a chromane-type derivative of abietic acid through quinomemethide intermediate.
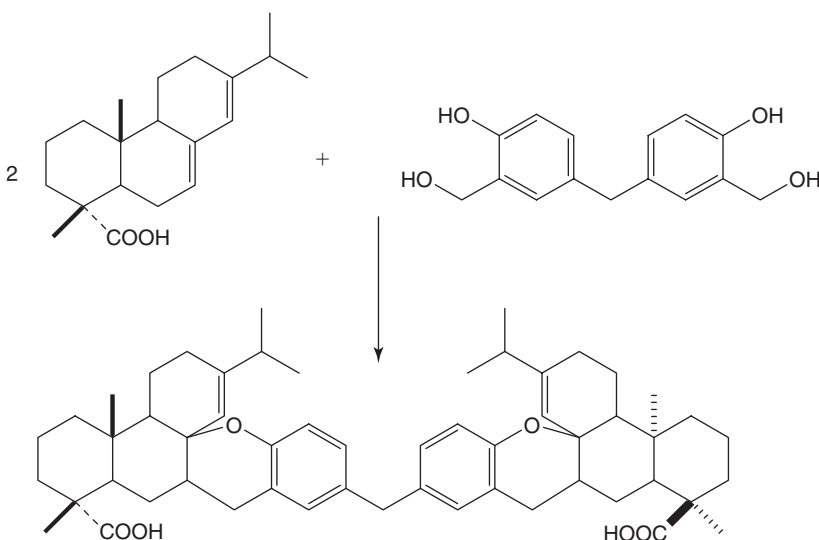
Figure 4.13   Formation of a chromane-type derivative of abietic acid by reaction with diphenylolpropane.

Another approach for the preparation of rosin-modified phenolics [33] involves the formation of quinoneme-thide by the reaction between phenol and formaldehyde, which then undergoes Diels–Alder addition with the less hindered abietic acid double bond forming a chromane-type derivative (Fig. 4.12).

Similar chromane structures (Fig. 4.13) can also be prepared by the reaction of abietic acid with dipheny-lolpropane [34].

Resins similar to those described in Fig. 4.11 were prepared by the reaction of abietic acid with aniline and for-maldehyde, with application in pressure-sensitive adhesives [35].

Levopimaric acid can also form a Diels–Alder adduct with formaldehyde [5, 36, 37] that can easily undergo acid cleavage to yield a 12-hydroxymethylabietic acid, which, in turn, can be converted into the corresponding 12-hydroxymethylabiet-8-enoic acid and 12-hydroxymethylabietol derivatives (Fig. 4.14). These hydroxymethyl-ated abietanols have been used as co-monomers in the synthesis of polyurethane [38, 39] and polyester [39] films and the corresponding alkoxylated derivatives in the preparation of polyurethane foams [40] and films [41].

Under strong acidic conditions and high temperatures, abietic-type acids can undergo dimerization [5, 42–44]. Although this transformation is frequently referred to as *polymerization*, the complex mixtures formed are pre-dominantly composed of dimers (Fig. 4.15), with minor amounts of trimers [45]. These rosin derivatives find applications in printing inks.
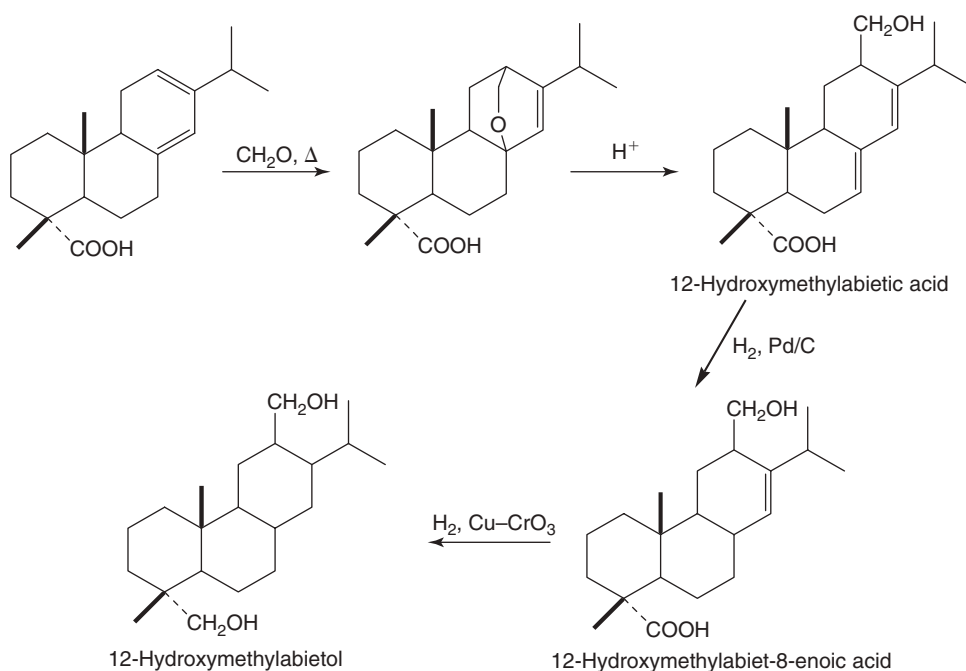
Figure 4.14 Formation of levopimaric adducts with formaldehyde and their conversion into 12-hydroxymethyl derivatives.
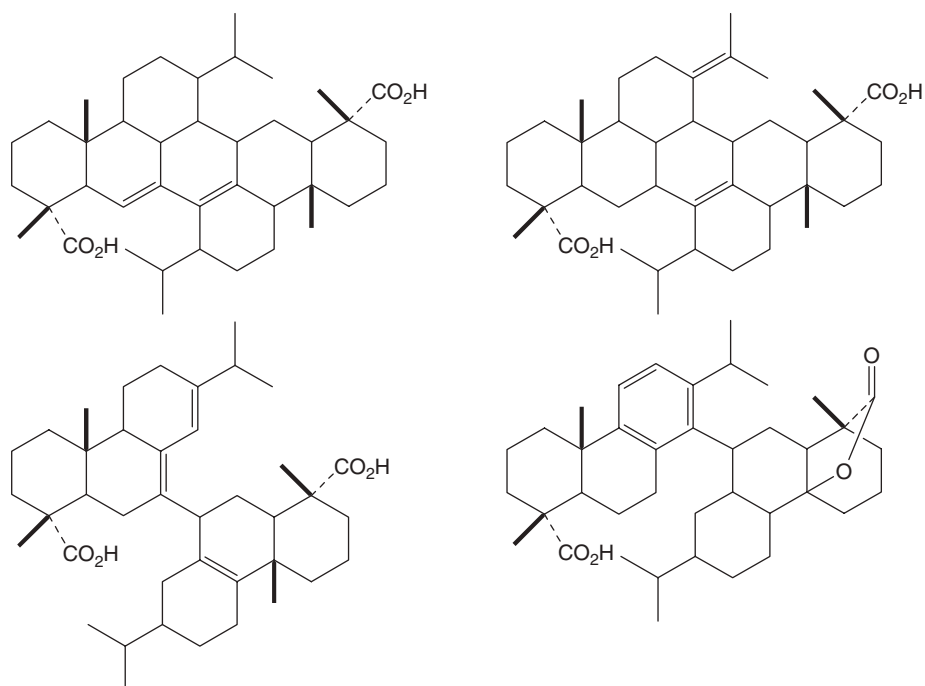
Figure 4.15 Typical dimeric structures of abietic-type acids.
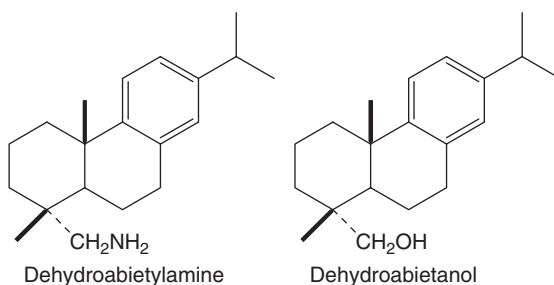
Figure 4.16   Structures of dehydroabietylamine and dehydroabietanol.

4.3.2   Reactions of the carboxylic group

Na, Mg, Ca, Zn, Al and ammonium resin acid salts are produced industrially [5], albeit their relative importance has been shifting with time because of changes in their relevant applications. Na, K and ammonium salts are partially water soluble and were used as soaps in the past. Presently, resin acids sodium salts are mainly used as intermediates in paper sizing.

The esterification of resin acids is carried out industrially at high temperatures (260–300°C) using metal oxides as catalysts. The most common commercially available esters are those with methanol and polyols like ethylene glycol, diethylene glycol, glycerol and pentaerythritol. Glycerol esters were the first to be used in protective coatings, although pentaerythritol esters are harder and more durable for varnishes. The methyl esters are normally used as plasticizing agents, as described below.

The alkoxylation of free resin acids with reagents such as ethylene oxide, yields hydroxyl-terminated esters which can easily undergo polymerization with an excess of ethylene oxide to produce polyethers of variable chain lengths [46]. These rosin derivatives can be used as chain extenders in the manufacture of polyurethane foams [46].

### 4.3.3   Miscellaneous reactions

Other chemical transformations involving the carboxylic group have been explored, although their practical interest remains marginal. Anhydrides can be prepared by refluxing the corresponding acid in acetic anhydride [5]. These derivatives have found modest applications as such (*e.g.* in paper sizing), but they are also useful as precursors to nitrogen derivatives [5]. Rosin amines can be prepared from the corresponding nitriles (Eq. 4.1) by the reaction of molten rosin with ammonia at high temperature [5]:

$$\text{RCOOH} + \text{NH}_3 \rightarrow [\text{RCONH}_2] \rightarrow \text{RCN} \rightarrow \text{RCH}_2\text{NH}_2 \tag{4.1}$$
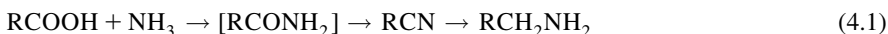
Dehydroabietylamine (Fig. 4.16) and the corresponding ammonium salts find a wide diversity of uses from cationic flotation agents to antioxidants, fungicides and anticorrosion materials [5].

The reduction of methyl dehydroabietate at high temperature leads to the formation of dehydroabietanol (Fig. 4.16), whose light colour and high stability make it a useful intermediate for the synthesis of a variety of esters used in protective coatings, adhesives and plasticizers [5].

4.4   MAJOR APPLICATIONS OF ROSIN AND DERIVATIVES

4.4.1   Paper sizing

Given the intrinsic hydrophylic character of cellulose fibres, specific additives are introduced into most papers to reduce this tendency to different extents according to their specific use, for example, to minimize the penetration of aqueous liquids, or the excessive wetting associated with certain printing processes [47]. This partial hydrophobization
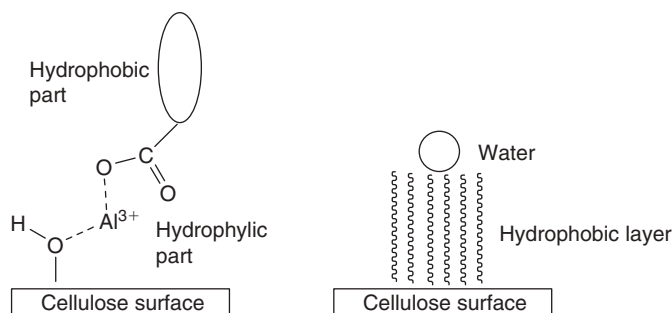
Figure 4.17 Interaction of aluminium resinates with cellulose surface.

can be achieved by bulk or surface treatment with adequate agents, which bind to the fibres' surface, either chemically or by other less strong interactions. This treatment is known as paper sizing. Among the numerous reagents tested for this purpose [48], three families dominate the actual industrial sizing namely, rosin and alum (aluminium sulphate), alkenyl succinic anhydrides (ASA) and alkyl ketene dimers (AKD) [47–50]. Sizing with rosin/alum was invented in 1807 [47, 49, 50] and had been the most important process up to the middle of the last century. However, the acidic conditions associated with its implementation was the main reason for its progressive abandonment because, on the one hand, cellulose degrades slowly by acid-catalyzed hydrolysis, thus inducing a progressive loss in the mechanical strength of the paper sheet and, on the other hand, acidic papers are incompatible with calcium carbonate, a very frequently used filler.

These problems provoked a steady decrease in the utilization of rosin alum in favour of the alternative use of AKD and ASA. However, since these sizing agents also have some drawbacks and are rather costly, research dealing with the implementation of rosin sizing under neutral conditions has been a continuous topic of investigation [48]. Rosin can be used in paper sizing in three forms, namely as sodium salts (known as neutral rosin), free rosin acids and modified rosin products. One of the most important rosin derivatives in this context is the maleopimaric acid adduct (Fig. 4.8), whose incorporation (8–15 per cent) into the sizing composition (a process referred to as "fortification") provides a marked improvement in efficiency compared with unmodified rosin [47]. Similar improvements can be achieved with fumaric or itaconic acid adducts, among others, although the maleopimaric acid adduct dominates the industrial applications of this family of agents.

Despite the increased hydrophilicity associated with the tricarboxylic functionality of the maleopimaric acid adduct, the corresponding increased anionicity reduces the tendency of the sizing agent to agglomerate and promotes a more uniform spreading over the sheet surface, while also increasing the reactivity with alum to form the corresponding aluminium rosinate, which is the actual sizing agent.

Several theories have been proposed to rationalize the mechanism of paper sizing with rosin [47, 49, 50]. An outline of the most relevant features involved in this process is provided here. Given that the cellulose surface is polar and negatively charged, the interaction with the sizing agent involves the *in situ* formation of an aluminium resinate, where the aluminium ions establish an electrostatic interaction between the negatively charged carboxylic groups of the resinate and the sheet surface (Fig. 4.17).

The uniform dispersion of the sizing agent over the cellulose surface, together with the alignment of the aliphatic triterpene skeletons away from the cellulose surface, creates a hydrophobic water-repellent layer (Fig. 4.17).

Effective sizing requires the presence of aluminium soluble complexes capable of exchanging one coordinating water molecule for a resinate anion, thus preserving the cationic nature of the ensuing species. An increase in the pH leads to a corresponding increase in the exchange between the coordinating water molecules and the hydroxy anions. Further water exchange with resinates can lead to the formation of neutral entities unable to interact with the cellulose surface, or, at even higher pH values, to the precipitation of aluminium hydroxide. This explains why sizing with rosin and alum is carried out normally in the pH range of 4–5.5 [49]. The inevitable requirements associated with rosin sizing at higher pH values are that, on the one hand, aluminium must remain in solution and, on the other hand, that its associated complexes are still cationic. The replacement of alum by other aluminium salts, such as polyaluminium chloride, was one of the first approaches in this context [48, 49]. Since then, many other additives have been tested in order to improve the cationicity of the aluminium species in neutral to basic conditions, so that rosin sizing can be applied to papermaking without the problems associated with acidity. Among them, nitrogen-containing

polymers, namely polyamines [51–53] and polyimines [54–57], sometimes in conjunction with rosin esters [58–61], have attracted much attention because of their considerable cationic charge in neutral conditions. Despite these and other recent endeavours [62–67], some authors are still sceptical about the viability of the use of rosin in neutral/alkaline sizing [54, 55].

4.4.2 Emulsification

Because of their amphiphilic character, alkali resinates have been exploited both as polymer latex stabilizers and as surfactants in emulsion polymerization from the early development of these techniques, as in the pre-Second World War industrial example of the polymerization of 2-chloro-1,3-butadiene, to produce neoprene [68]. In the following decades, other emulsion polymerizations systems, like the synthesis of styrene–butadiene copolymers [68, 69], also called upon these surfactants, which are still being envisaged today, for example, for the polymerization of styrene [70] and chloroprene [71]. However, the reactivity of the conjugated double bond towards free radicals has made it more profitable to use hydrogenated or dehydrogenated rosins rather than their natural forms [68, 72].

4.4.3 Adhesive tack

As with most of the other sections of this chapter, the basic reference to the applications of rosin and its derivatives as components of adhesive formulations up to the mid-1980s, is the corresponding chapter by Kennedy *et al.* [73] of the classical Naval Store book. The major emphasis in that chapter was placed on the tackifying properties of rosin-based resins in pressure-sensitive, hot melt and sealant adhesives. Therefore, before proceeding to a critical bibliographic survey, it seems appropriate to define the concept of tack and its repercussion in the broad area of adhesion, as opposed to other contexts, like printing inks, paints and coatings.

Adhesive tack is the property that controls the instantaneous formation of a bond when an adhesive and a surface are brought into contact. In other words, tack is a measure of the "stickiness" of an adhesive while still in a liquid or viscoelastic state, or simply the resistance to separation which is rate and temperature dependent and involves viscoelastic deformation of the bulk adhesive. The appropriate measurement is the work expended in separation, rather than the force used. The critical features of tack are characterized by the "wetting stage", controlled by the surface energy, viscosity and thickness of the adhesive, and the debonding stage (peel strength), which is strongly influenced by the viscoelastic response of the adhesive. Although tack tests are generally simple to perform, this parameter lacks a strict physical definition or unit and the values obtained on a given apparatus are self-consistent, but not comparable with those from a different measuring system. Maximum tack occurs when the conditions of measurement and the properties of the tacky material combine to have a high energy loss within the adhesive material. This is the basis for the formulation and incorporation of "tackifiers" in adhesive formulations.

In the empirical world of tack experts, many professional terms are employed, like "green strength" (as initial tack is sometimes called), which relate to the resistance to separation before the adhesive has had a chance to vulcanize or crosslink. This characteristic may also be called "quick tack" or "aggressive tack". It may be one of the most important properties in determining the suitability of an adhesive, such as that placed on a pressure-sensitive tape, for a certain application. Associated with tack is "dry tack", which is a property of certain adhesives to stick to one another even though they seem to be dry to the touch. Autohesive tack (or autohesion) is the dry tack between materials having similar chemical compositions. "Tack range" is the time that an adhesive will remain in a tacky condition.

The relative decline in interest in using rosin as a tackifier in adhesive formulations, clearly reflected by the paucity of publications up to the mid-1990s, is counterbalanced by a dramatic increase in the number of papers published in the last decade in scientific and technical journals (more than 50), as predicted by an editorial in Chemical Week in 1995 [74]. A selection from this large output is given here to summarize some of the most salient features arising from the return to the utilization of this renewable resource as a key adhesive component.

A study of the surface properties of pentaerythritol rosin ester [75] showed that the most abundant moieties crowding this surface are the ester groups and that the surface energy was composed of a dispersive contribution of $\sim$22 mJ m^{-2} and a polar one of $\sim$10 mJ m^{-2}. This relatively low surface tension, compared with that of many polar polymers and indeed with most surfaces to be glued, explains in part the tackifying role of rosin derivatives added to polymer adhesive bases.

Rosin esters have been incorporated into a variety of macromolecules with potential adhesive properties in order to enhance their tack and in many of these studies the beneficial effect was compared with that of terpene and hydrocarbon resins. The polymer substrates include ethylene–vinyl acetate copolymers [76–78], natural rubber [79] and thermoplastic elastomers [80, 81], polyurethanes, where the rosin derivatives participate chemically in the polymer growth [82, 83] and acrylic resins in organic media [84] and as water emulsions [85]. Pressure-sensitive adhesives as well as hot melts were thus characterized in terms of tack and peel strength as a function of a variety of parameters, including the composition and average molecular weight of the base polymer, the amount of added tackifier and its miscibility in the polymer. Rosin esters gave satisfactory results with most polymers after the appropriate optimization of the adhesive compositions and compared favourably with other natural (terpenic) and synthetic (petroleum-based oligomers) tackifiers.

Some rosin derivatives have been found to provoke allergies [86], particularly if they are present in curative plasters.

4.4.4 Polymer chemistry and processing

Maiti *et al.* [2] thoroughly reviewed the technical literature up to the late 1980s related to the use of rosin and its derivatives as monomers or co-monomers in a variety of polymerization systems, as well as the properties of the ensuing polymers. Most of the documents cited in this monograph were patents unavailable to us, whose scientific content was therefore difficult to judge, but nonetheless, the interest of this survey lies in the fact that it emphasizes the extensive search of materials based on rosin. Some clear-cut investigations in this context are described here as typical examples of the exploitation of rosin and its derivatives as polymer precursors.

Maleopimaric anhydride can react with amines to form maleimides. If diamines are used, the corresponding maleimide-amines can be polymerized through a step process (Fig. 4.18), involving the condensation of the carboxylic moiety with the primary amine to form a poly(amide-imide), which was used in the formulation of gravure printing inks [87].

These poly(amide-imide) materials were extensively studied in the 1980s in various aspects (*e.g.* synthesis and preparation of blends with other polymeric materials), [2, 88–96] demonstrating the increasing interest in these materials. More recently, water soluble polyamides and poly(amide-imide)s [97] as well as polyhydroxyimides [98] structurally analogous to those described in Fig. 4.18 have been reported. Additionally, photoactive polymers were prepared by the condensation of a maleopimaric adduct with azo-dye type diamines [99]. The levopimaric
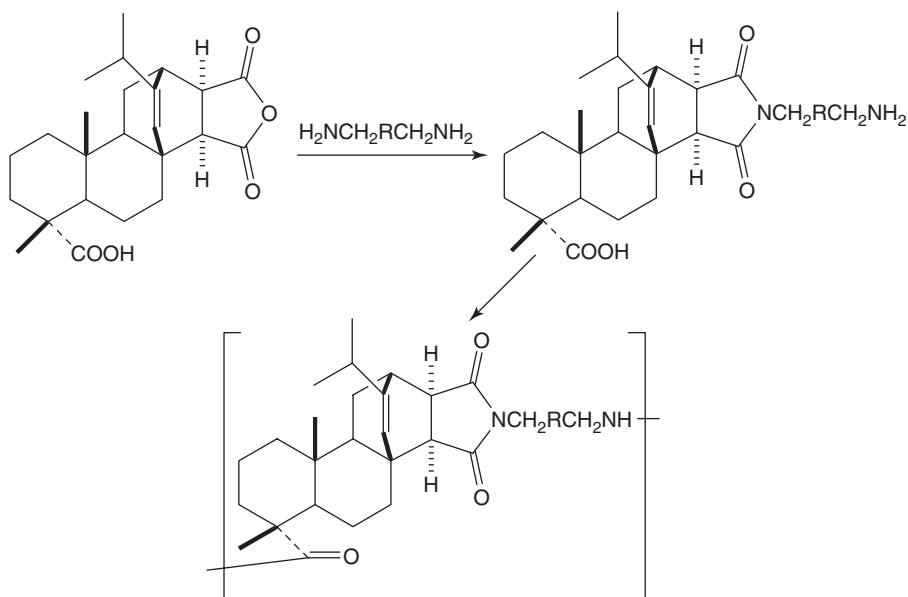
Figure 4.18   Synthesis and polycondensation of a rosin-based poly(amide-imide).

adduct with acrylic acid has been used as a polycondensation monomer, both as a diacid in the synthesis of poly-esters [2, 100] and, after conversion of its two carboxylic groups into isocyanate functions, as a co-monomer in the preparation of polyurethanes [101].

Maleopimaric acid and its anhydride were converted into the corresponding peroxides with the aid of an organic peroxide and used as reactive compatibilizers in the extrusion of polyethylene and polyamide 6 [102]. The ensuing blends showed improved mechanical properties compared with those of physical mixtures of the two polymers, suggesting that the rosin-based peroxide had indeed played an active role in enhancing the quality of the interface between the two polymers.

The maleopimaric and acrylopimaric adducts, after a three-step synthesis with ethylene glycol catalyzed by *p*-toluene sulphonic acid (*p*TSA), followed by epychlorydrine and by acrylic or methacrylic acid, led to the forma-tion of vinyl-type ester monomers (Fig. 4.19), which were then submitted to radical copolymerization with styrene and tested as metal coatings [103]. A similar approach to coating materials was recently applied to prepare unsat-urated polyester resins based on resin acid adducts, glycols and maleic anhydride [104, 105].
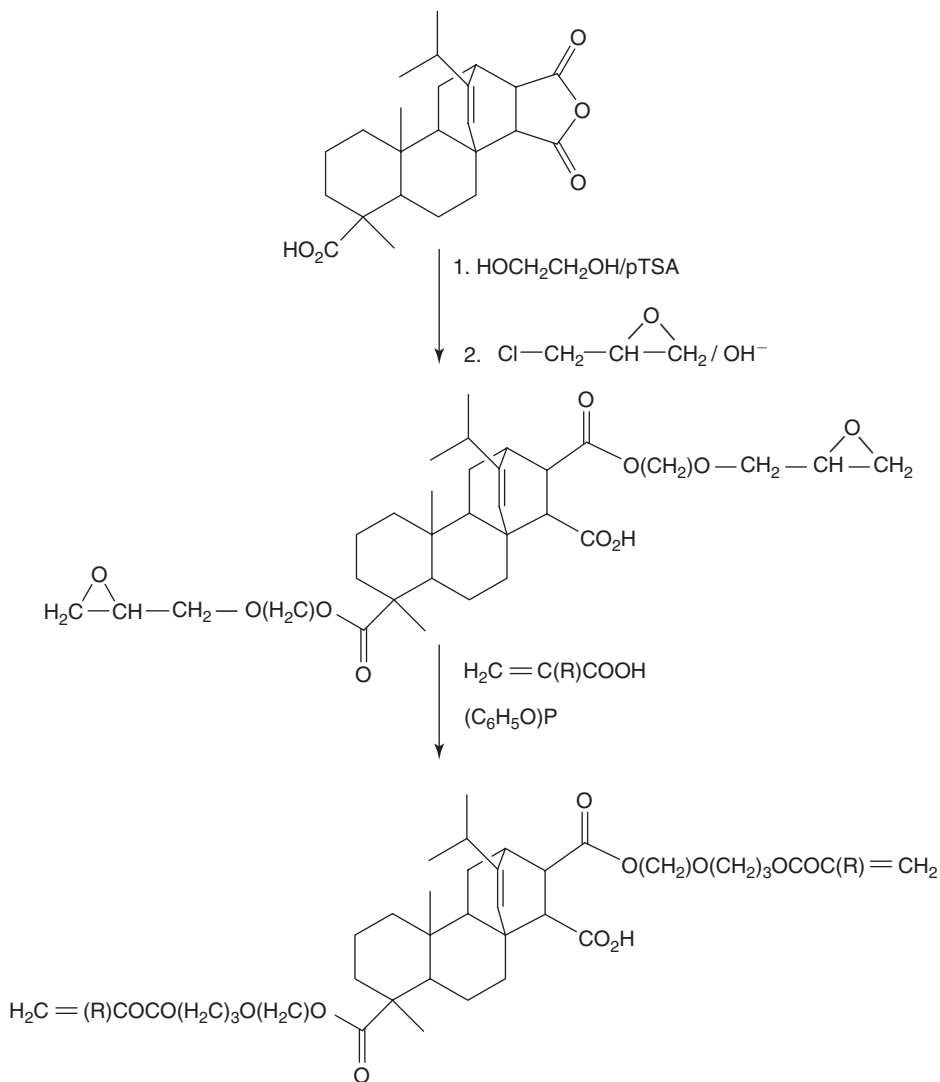
Figure 4.19 Synthesis of vinyl-type ester monomers from the maleopimaric adduct [103].

As shown above (Fig. 4.9), maleopimaric anhydride can be converted into diallyl derivatives [25], which can be further converted into dimeric-type ketones [27]. Both intermediates were used in polymerization tests that yielded crosslinked materials [25, 27].

When resin acid ketone dimers [26] (bisdienes) were submitted to the Diels–Alder reaction with an aromatic bismaleimide [106], high molecular weight thermally stable polyimides were obtained (Fig. 4.20). Similar materials were also prepared using resin acid dimers and aliphatic bismaleimides, as well as bisacrilamides [107]. Acrylonitrile adducts with resin acid dimers were also used as intermediates for the synthesis of polyamides with aliphatic diamines [108].

Resin acid dimer adducts with maleic anhydride and acrylic acid were also used to prepare epoxy resins [107, 109]. The epoxy precursors were prepared by the reaction of the Diels–Alder adducts with di(ethanol)amine, followed by treatment with epychlorydrine under alkaline conditions, as shown in Fig. 4.21 for the acrylic acid adduct [109]. After curing, the ensuing materials produce high stability coats [109].

On a different approach, poly(4-abietylmethylstyrene) was prepared in high yields by the reaction of poly (4-chloromethylstyrene) with sodium abietate. Near-UV irradiation of this novel polymer induced its crosslinking by photodimerization through the conjugated double bonds of the abietate moieties [110], presumably by the formation of dimeric structures similar to those described in Fig. 4.15. Abietic acid dimers were also used as diacids in the synthesis of polyamides by reaction with diamines [111].

Rosin and its derivatives are frequently used as polymer additives in different capacities. Their role as plasticizers is illustrated by recent work related to the paper coating for food packaging with a 3-hydroxybutirate/3-hydroxyvalerate copolymer (PHB/V) [112, 113]. The addition of tall oil rosin to the copolymer was found to improve its water vapour barrier properties as well as to reduce the pinhole density of the corresponding laminated papers.
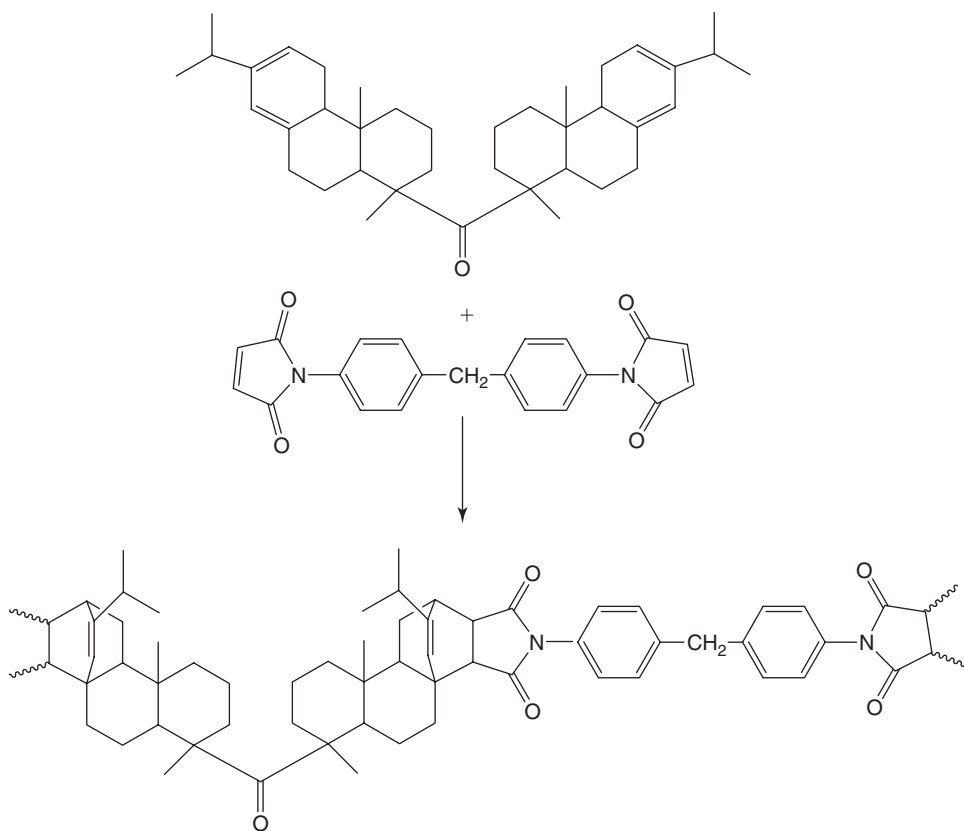
Figure 4.20 Synthesis of polyimides by Diels–Alder condensation of resin acid dimers with aromatic bismaleimides [106].
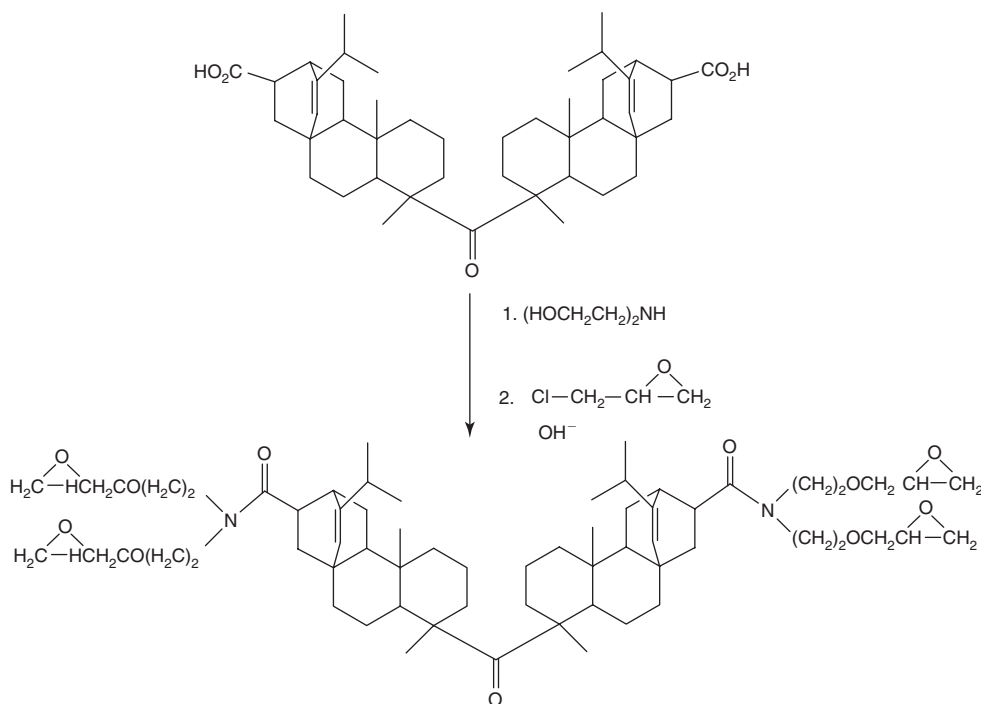
Figure 4.21 Synthesis of epoxy resins from resin acid dimer adduct with acrylic acid.

Dialkyl ketones: R_1 = Alkyl, R_2 = Alkyl'
Aryl aldehydes: R_1 = Aryl, R_2 = H
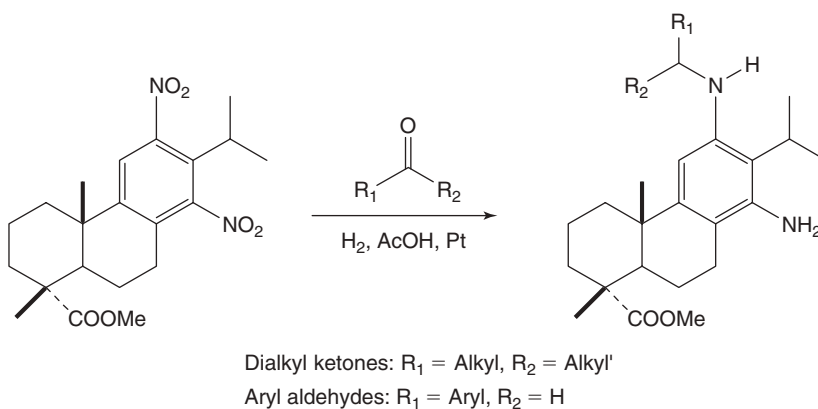
Figure 4.22 Synthesis of secondary amines of methyl dehydroabietate.

In another vein, secondary amines prepared by the reductive amination of appropriate carbonyl compounds with methyl 12,14-dinitrodehydroabietate (Fig. 4.22) gave promising results when used as stabilizers against thermal, photochemical and oxidative degradation of low-density polyethylene and ethylene–propylene elastomers [114–116]. This active role is not surprising given the well-known fact that aromatic amines are excellent free radical traps.

4.4.5 Printing inks

Four distinct processes dominate the printing technology [117], namely (i) offset lithography, by far the most important, (ii) letterpress, (iii) flexography and (iv) gravure. A description of the principles and peculiarities associated with

each of them falls outside the scope of this chapter. In relation to their ink requirements, the major difference lies in the viscosity, which must be very high for the first two processes (paste inks) and low for the other two (liquid inks). Interestingly, although the properties of rosin itself do not make it very viable as a component of any of these inks, several of its derivatives have been, and are being, extensively used in the manufacture of all four types of printing inks. The reader is invited to consult Burke's chapter in the Naval Store book [34] for what is still the best available monograph on the use of rosin compounds in printing inks, even compared with the latest edition of the Printing Ink Manual [117]. It provides a clear technical introduction to the relationship between printing processes and the requirement of the corresponding inks, a thorough description of the types and roles of the rosin derivatives in each family of inks and a detailed literature survey up to the mid-1980s.

Any ink (varnish) must be transferred from the printing surface to the substrate to be printed (varnished) while still in a fluid state and thereafter it must dry through an appropriate physical or chemical process and turn into a solid film. The film-forming aptitude of an ink (varnish) is thus of paramount importance, as are the properties of the dried film. In the search for an optimal resin composition (the film precursor), these qualities represent therefore the first priority, but the solutions are not universal, for they must comply with the nature of the printing process. Since the only difference between an ink and a varnish is the presence of a suspended pigment in the former, the composition of the liquid phase is the same in both instances, for a given printing and drying process.

The most important rosin derivatives used in printing ink formulations are rosin oligomers and their esters, metal resinates, modified phenolic and alkyd resins, ester gums, maleic and fumaric acid adducts and their esters. Practically all types of printing inks can be manufactured with rosin-based components, because they provide good miscibility and compatibility with most film formers and other ink additives.

The following succinct account of the major utilizations of rosin derivatives in printing inks is aimed at giving a mere introduction to the art, which can be enriched by looking up the more comprehensive treatments already quoted [34, 117]. In contrast with the applications related to adhesion and tack, which are thoroughly documented by the numerous studies discussed in the preceding section, research dealing with printing ink formulations is much more confidential and the corresponding open documents are few and far between. It follows that the brief survey below is only based on general technical reports.

The high acid content of rosin and its oligomers may be lowered by reacting them with lime, calcium acetate or zinc oxide, or indeed a combination of these compounds. The ensuing metal resinates have high softening temperatures and are therefore inclined to give brittle films. When used in conjunction with a polymeric film former, like cellulose esters, in gravure inks, good rub and abrasion resistance are achieved, together with a reduction in green tack. Their incorporation in lithographic inks provides good pigment wetting and prevents gelation during the storage of drying oil varnishes.

Of the numerous rosin-based esters used in printing inks, the simplest are those formed by the direct condensation reaction of rosin or its oligomers with glycerol and pentaerythritol at high temperature. They find applications in letterpress and lithographic inks and are gaining use also in liquid ink compositions. The other ester family comprises the rosin adducts with maleic and fumaric acids and their esters. They are usually classified according to their solubility in different organic media. The lower their acid values (free COOH groups), the higher their solubility in non-polar solvents and vice versa. They are widely used in printing inks; in particular, high acid-value maleics are incorporated into water- and moisture-set letterpress inks and into water-based flexographic inks in conjunction with an amine or ammonia. Medium acid-value counterparts are added into alcohol-based gravure and flexographic inks in combination with polyamides or cellulose derivatives. Hydrocarbon soluble resins (low acid value) have the advantage of possessing a very pale coloration and are employed as additives to letterpress and lithographic gloss inks, heatset inks and overprint varnishes.

The third large group of rosin-based materials that are widely used in printing ink formulations are rosin-modified phenolic resins (*e.g.* Figs 4.11 and 4.13) and their esters. With their variety of properties, depending on the actual chemical composition, they represent an important family of materials in printing ink technology. The variables that allow such a diversity of properties to be obtained are (i) the actual phenol homologue, (ii) the classical phenol (P)/formaldehyde (F) ratio, (iii) the relative amount of PF resin with respect to rosin, (iv) the use and amount of a dicarboxylic acid structural modifier and (v) the final esterification (if any) in terms of both its extent and the type of polyol used. Typically, rosin is added to a PF prepolymer and the ensuing mixture is heated at 100–150°C in the presence of a basic catalyst. The temperature is then increased to ~200°C to complete the mutual condensation. If a high acid functionality is desired, the resin is then treated with a dicarboxylic acid. Finally, polyols like glycerol and pentaerythritol can be used in a further step to esterify some or most of the resin free COOH groups, in order to achieve different properties. Rosin-modified PF resins possess many specific properties, valuable in different printing

ink types, as a function of their composition. They are compatible with alkyd resins and most modifiers used in oil-based inks and tend to give tough, glossy dry films with good resistance.

A recent interesting addition to this realm is the use of rosin-based resins in the manufacture of the new generation of ink jet inks, the phase-change inks [118].

4.4.6   Miscellaneous applications

The controlled release of pharmaceuticals and agrochemicals is a highly active research topic because, on the one hand, it contributes to maintain for long periods the constant levels required for effective disease treatment or pest control and, on the other hand, it sharply reduces the administered doses, with the concomitant health, environmental and economical benefits. Rosin and rosin esters (*e.g.* rosin and maleic rosin esters with glycerol, sorbitol, mannitol and pentaerythritol) have been investigated in the last couple of decades as coatings [119–123] and micro-encapsulating materials [83–91] for the controlled release of several pharmaceuticals, and as implant matrix for the delivery of drugs [124], given their established *in vitro* and *in vivo* degradation behaviour and biocompatibility [125]. Although rosin and hydrogenated rosin films tend to pose handling problems because of their brittle nature, this drawback can be easily overcome by adding adequate hydrophobic plasticizers (up to 20 per cent w/w), such as tributil sebacate and tributil citrate [125, 126].

Recent studies also indicated that rosin nanoparticles can be effective for the encapsulation and delivery of drugs [127]. Rosin formulations have also been used in the controlled release of carbofurane nematicides, thus allowing the applied doses to be reduced by half and to increase significantly their effectiveness and availability in the soil over longer periods of time [128].

Other applications of rosin derivatives and polymers include emulsifiers for pharmaceuticals and cosmetics [129, 130], flotation oils in the phosphate industry [131] and the formulation of polymer-concrete composites for the construction of temporary and semi-permanent military structures in arid zones [132].

4.5   CONCLUDING REMARKS

As in the case of other traditional renewable resources exploited by mankind since the inception of elementary technologies, for example, gelatin, soaps and vegetable oils, rosin and its derivatives suffered a decline in their utilization with the boom of petrochemistry in the second half of the last century. The renewed interest in these natural products is a growing reality because of the increasing awareness of the need to replace fossil resources with renewable counterparts. This inversion of tendency has already become visible in the case of rosin by the recent surge in publications devoted to the search both for more viable applications of known processes and commodities and for new materials with improved properties for razor-edge technologies.

REFERENCES

1. Zinkel D.E., Russel J., *Naval Stores. Production, Chemistry, Utilization*, Pulp Chemical Association, New York, 1989.
2. Maiti S., Ray S.S., Kundu A.K., Rosin – A renewable resource for polymers and polymer chemicals, *Prog. Polym. Sci.*, **14**(3), 1989, 297–338.
3. Stauffer D.F., Production, markets and economics, in *Naval Stores. Production, Chemistry, Utilization* (Eds. Zinkel D.F. and J. Russel , Pulp Chemical Association, New York, 1989, pp. 39–82.
4. Coppen J.J.W., Hone G.A., *Gum Naval Stores: Turpentine and Rosin from Pine Resin*, FAO, Rome, 1995.
5. Soltes J., Zinkel D.F., Chemistry of rosin, in *Naval Stores. Production, Chemistry, Utilization* (Eds. Zinkel D.F. and Russel J.), Pulp Chemical Association, New York, 1989, pp. 261–345.
6. Stump J.H., Quality control (tall oil, rosin, and fatty acids), in *Naval Stores. Production, Chemistry, Utilization* (Eds. Zinkel D.F. and Russel J.), Pulp Chemical Association, New York, 1989, pp. 846–868.
7. Schuller W.H., Lawrence R.V., Oxidation of levopimaric acid pine gum and various rosins with singlet oxygen, *Ind. Eng. Chem. Prod. Res. Develop.*, **6**(4), 1967, 266–268.
8. Fleck E.E., Palkin S., On the nature of pyroabietic acids, *J. Am. Chem. Soc.*, **60**, 1938, 921–925.
9. Fleck E.E., Palkin S., The dihydroabietic acids from so-called pyroabietic acids, *J. Am. Chem. Soc.*, **60**, 1938, 2621–2622.
10. Fleck E.E., Palkin S., The composition of so-called pyroabietic acid prepared without catalyst, *J. Am. Chem. Soc.*, **61**, 1939, 247–249.

11. Fleck E.E., Palkin S., The presence of dihydroabietic acid in pine oleoresin and rosin, *J. Am. Chem. Soc.*, **61**, 1939, 1330–1332.
12. Fieser L., Campbell W., Substitution reactions of dehydroabietic acid, *J. Am. Chem. Soc.*, **60**, 1938, 2631–2636.
13. Fieser L., Campbell W., Hydroxyl and amino derivatives of dehydroabietic acid and dehydroabietinol, *J. Am. Chem. Soc.*, **61**, 1939, 2528–2534.
14. Campbell W., Morgana M., Substitution reactions of dehydroabietic acid. II, *J. Am. Chem. Soc.*, **63**, 1941, 1838–1843.
15. Levinson A.S., Mononitration of methyl abieta-8,11,13-trien-18-oate, *J. Org. Chem.*, **36**(20), 1971, 3062–3064.
16. Gigante B., Prazeres A.O., Marcelocurto M.J., Mild and selective nitration by claycop, *J. Org. Chem.*, **60**(11), 1995, 3445–3447.
17. Schuller W.H., Lawrence R.V., Base-catalyzed isomerization of resin acids, *J. Org. Chem.*, **30**(6), 1965, 2080–2082.
18. Takeda H., Kanno H., Schuller W.H., Lawrence R.V., Effect of temperature on rosins and pine gum, *Ind. Eng. Chem. Prod. Res. Develop.*, **7**(3), 1968, 186–189.
19. Takeda H., Schuller W.H., Lawrence R.V., Thermal isomerization of methyl abietate, *J. Chem. Eng. Data*, **13**(4), 1968, 579–581.
20. Takeda H., Schuller W.H., Lawrence R.V., Thermal isomerization of abietic acid, *J. Org. Chem.*, **33**(4), 1968, 1683–1684.
21. Takeda H., Schuller W.H., Lawrence R.V., Thermal behavior of some resin acid esters, *J. Chem. Eng. Data*, **14**(1), 1969, 89–90.
22. Portugal I., Vital J., Lobo L.S., Resin acids isomerization – A kinetic-study, *Chem. Eng. Sci.*, **47**(9–11), 1992, 2671–2676.
23. Lloyd W.D., Hedrick G.W., Diels–Alder reaction of levopimaric acid and its use in quantitative determinations, *J. Org. Chem.*, **26**(6), 1961, 2029–2032.
24. Kotsuki H., Kataoka M., Matsuo K., Suetomo S., Shiro M., Nishizawa H., High-pressure organic-chemistry. 17. Diels–Alder reaction of methyl palustrate with maleic-anhydride and *N*-phenylmaleimide, *J. Chem. Soc. Perkin Trans. I*, **22**, 1993, 2773–2776.
25. Bicu I., Mustata F., Allylic polymers from resin acids, *Angew. Makromol. Chem.*, **246**, 1997, 11–22.
26. Bicu I., Mustata F., Study of the condensation products of abietic acid with formaldehyde at high-temperatures, *Angew. Makromol. Chem.*, **222**, 1994, 165–174.
27. Bicu I., Mustata F., Allylic polymers from resin acids – Monomer synthesis at high temperature, *Angew. Makromol. Chem.*, **255**, 1998, 45–51.
28. Minor J.C., Lawrence R.V., Esterification of methylolated rosin, *Ind. Eng. Chem.*, **50**(8), 1958, 1127–1130.
29. Royals E.E., Pyrolysis of esters. 1. Nonselectivity in the direction of elimination by pyrolysis, *J. Org. Chem.*, **23**(11), 1958, 1822.
30. Black D.K., Hedrick G.W., Condensation of paraformaldehyde with abietic acid and some of its derivatives, *J. Org. Chem.*, **32**(12), 1967, 3763–3767.
31. Stclair W.E., Minor J.C., Lawrence R.V., Fused metal resinates from aldehyde-modified rosin, *Ind. Eng. Chem.*, **46**(9), 1954, 1973–1976.
32. Bicu I., Mustata F., Study of the condensation products of abietic acid with formaldehyde, *Angew. Makromol. Chem.*, **213**, 1993, 169–179.
33. Hultzsch K., Uber Zusammenhange Und Abgrenzungen Bei Poly-Reaktionen, *Angew. Chem.*, **64**(13), 1952, 361.
34. Burke R.E., Rosin-based printing inks, in *Naval Stores. Production, Chemistry, Utilization* (Eds. Zinkel D.F. and J. Russel , Pulp Chemical Association, New York, 1989, pp. 667–700.
35. Mustata F., Bicu I., Epoxy aniline formaldehyde resins modified with resin acids, *Polimery*, **46**(7–8), 2001, 534–539.
36. Parkin B.A., Hedrick G.W., Chemistry of resin acids. I. Reaction of levopimaric acid with formaldehyde, *J. Org. Chem.*, **30**(7), 1965, 2356–2358.
37. Parkin B.A., Summers H.B., Settine R.L., Hedrick G.W., Production of levopimaric acid–formaldehyde adduct and hydroxymethylated materials from resin acids and rosin, *Ind. Eng. Chem. Prod. Res. Develop.*, **5**(3), 1966, 257–262.
38. Lewis J.B., Hedrick G.W., Hydroxymethylated derivatives of resin acids – Use in polyurethane films, *Ind. Eng. Chem. Prod. Res. Develop.*, **9**(3), 1970, 304–310.
39. Osman M.A., Marvel C.S., Polyesters from 12-hydroxymethyltetrahydroabietic acid and 12-hydroxymethyltetrahydroabietanol, *J. Polym. Sci. A1 Pol. Chem.*, **9**(5), 1971, 1213–1218.
40. Rohde W.A., Black D.K., Hedrick G.W., Resin–formaldehyde reaction – Separation of hydroxymethylated derivatives of resin acids, *Ind. Eng. Chem. Prod. Res. Develop.*, **12**(3), 1973, 241–246.
41. Bingham J.F., Marvel C.S., Polymers containing 12-hydroxymethyltetrahydroabietanol, *J. Polym. Sci. A1 Pol. Chem.*, **10**(2), 1972, 489–496.
42. Parkin B.A., Schuller W.H., Catalyst–solvent systems for dimerization of abietic acid and rosin, *Ind. Eng. Chem. Prod. Res. Develop.*, **11**(2), 1972, 156–158.
43. Parkin B.A., Schuller W.H., Polymerized rosin – Continuous method, *Ind. Eng. Chem. Prod. Res. Develop.*, **12**(3), 1973, 238–240.
44. Parkin B.A., Schuller W.H., Lawrence R.V., Thermal dimerization of rosin, *Ind. Eng. Chem. Prod. Res. Develop.*, **8**(3), 1969, 304–306.

45. Chang T.L., Analysis of tall oil by gel permeation chromatography, *Anal. Chem.*, **40**(6), 1968, 989–992.
46. Rohde W.A., Hedrick G.W., Esters of rosin acids and glycidyl ethers, *J. Am. Oil Chem. Soc.*, **47**(1), 1970, 3–4.
47. Niemo L., Internal sizing of paper, in *Papermaking Chemistry* (Ed. Niemo L.), Tappi Press, Helsinki, 1999.
48. Roberts J.C., Neutral and alkaline sizing, in *Paper Chemistry* (Ed. Roberts J.C.), Blackie Academic & Professional, London, 1996, pp. 140–160.
49. Gess J.M., The sizing of paper with rosin and alum at acid pHs, in *Paper Chemistry* (Ed. Roberts J.C.), Blackie Academic and Professional, Glasgow, 1996, pp. 120–139.
50. Strazdins E., Paper sizes and sizing, in *Naval Stores. Production, Chemistry, Utilization* (Eds. Zinkel D.F. and Russel J.), Pulp Chemical Association, New York, 1989, pp. 575–624.
51. Wu Z.H., Tanaka H., Behaviors of polyvinylamines in neutral rosin sizing, *Mokuzai Gakkaishi*, **41**(10), 1995, 911–916.
52. Wu Z.H., Chen S.P., Tanaka H., Effects of polyamine structure on rosin sizing under neutral papermaking conditions, *J. Appl. Polym. Sci.*, **65**(11), 1997, 2159–2163.
53. Wu Z.H., Chen S.P., Functions of polyamines in rosin sizing under neutral papermaking conditions, *Chin. J. Polym. Sci.*, **19**(2), 2001, 217–221.
54. Hartong B., Deng Y., Evidence of ester bond contribution to neutral to alkaline rosin sizing using polyethyleneimine–epichlorohydrin as a mordant, *J. Pulp Paper Sci.*, **30**(7), 2004, 203–209.
55. Xu Y., Hartong B., Deng Y., Neutral to alkaline rosin sizing using polyethyleneimine-epichlorohydrin (PEI-epi) as a mordant, *J. Pulp Pap. Sci.*, **28**(2), 2002, 39–44.
56. Zhuang J.F., Biermann C.J., Neutral to alkaline rosin soap sizing with metal-ions and polyethylenimine as mordants, *Tappi J.*, **78**(4), 1995, 155–162.
57. Biermann C.J., Rosin sizing with polyamine mordants from pH 3 to 10, *Tappi J.*, **75**(5), 1992, 166–171.
58. Li H.J., Ni Y.H., Sain M., Further understanding on polyethyleneimine-induced rosin ester sizing, *Nord. Pulp Pap. Res. J.*, **18**(1), 2003, 5–9.
59. Wang F., Kitaoka T., Tanaka H., Supramolecular structure and sizing performance of rosin-based emulsion size microparticles, *Coll. Surf. A Physicochem. Eng. Aspects*, **221**(1–3), 2003, 19–28.
60. Ito K., Isogai A., Onabe F., Rosin–ester sizing for alkaline papermaking, *J. Pulp Pap. Sci.*, **25**(6), 1999, 222–226.
61. Ito K., Isogai A., Onabe F., Retention behavior of size and aluminum components on handsheets in rosin–ester size alum systems, *J. Wood Sci.*, **45**(1), 1999, 46–52.
62. Kitaoka T., Isogai A., Onabe F., Endo T., Sizing mechanism of rosin emulsion size-alum systems. Part 4. Surface sizing by rosin emulsion size on alum-treated base paper, *Nord. Pulp Pap. Res. J.*, **16**(2), 2001, 96–102.
63. Wang F., Tanaka H., Mechanisms of neutral-alkaline paper sizing with usual rosin size using alum-polymer dual retention aid system, *J. Pulp Pap. Sci.*, **27**(1), 2001, 8–13.
64. Wang F., Wu Z.H., Tanaka H., Preparation and sizing mechanisms of neutral rosin size II: Functions of rosin derivatives on sizing efficiency, *J. Wood Sci.*, **45**(6), 1999, 475–480.
65. Wang T., Simonsen J., Biermann C.J., A new sizing agent: Styrene-maleic anhydride copolymer with alum or iron mordants, *Tappi J.*, **80**(1), 1997, 277–282.
66. Matsushita Y., Iwatsuki A., Yasuda S., Application of cationic polymer prepared from sulfuric acid lignin as a retention aid for usual rosin sizes to neutral papermaking, *J. Wood Sci.*, **50**(6), 2004, 540–544.
67. Wang F., Kitaoka T., Tanaka H., Vinylformamide-based cationic polymers as retention aids in alkaline papermaking, *Tappi J.*, **2**(12), 2003, 21–26.
68. Davis C.B., Rosin soaps as polymerization emulsifiers, in *Naval Stores. Production, Chemistry, Utilization* (Eds. Zinkel D.F. and Russel J.), Pulp Chemical Association, New York, 1989, pp. 625–644.
69. Carr C.W., Kolthoff I.M., Meehan E.J., Williams D.E., Studies on the rate of the emulsion polymerization of butadiene–styrene (75–25) as a function of the amount and kind of emulsifier used. 2. Polymerizations with fatty acid soaps, rosin soaps, and various synthetic emulsifiers, *J. Polym. Sci.*, **5**(2), 1950, 201–206.
70. Mayer M.J.J., Meuldijk J., Thoenes D., Emulsion polymerization of styrene with disproportionated rosin acid soap as emulsifier, *J. Appl. Polym. Sci.*, **59**(6), 1996, 1047.
71. Cochet F., Claverie J.P., Graillat C., Sauterey F., Guyot A., Emulsion polymerization of chloroprene in the presence of a maleic polymerizable surfactant: Control of gel formation at low conversion, *Macromolecules*, **37**(11), 2004, 4081–4086.
72. Zucolotto M., Darocha E.C., Vonholleben M.L.A., Disproportionation of rosin from pinus-elliotti – Obtention of emulsifier for polymerization, *Quim. Nova*, **18**(1), 1995, 78–79.
73. Kennedy N.L., Krajca K.E., Russel J., Rosin in adhesive tackifiers, in *Naval Stores. Production, Chemistry, Utilization* (Eds. Zinkel D.F. and Russel J.), Pulp Chemical Association, New York, 1989, pp. 645–664.
74. Fattah H., Adhesives and sealants – Rosin resin makers fight back, *Chem. Week*, **158**(45), 1996, 45.
75. Comyn J., Surface characterization of pentaerythritol rosin ester, *Int. J. Adhes. Adhes.*, **15**(1), 1995, 9–14.
76. Shih H.H., Hamed G.R., Peel adhesion and viscoelasticity of poly(ethylene-co-vinyl acetate)-based hot melt adhesives. 1. The effect of tackifier compatibility, *J. Appl. Polym. Sci.*, **63**(3), 1997, 323–331.

77. Takemoto M., Karasawa T., Mizumachi H., Kajiyama M., Miscibility between ethylene vinyl acetate copolymers and tackifier resins, *J. Adhesion*, **72**(1), 2000, 85–96.

78. Barrueso-Martinez M.L., Ferrandiz-Gomez T.D., Romero-Sanchez M.D., Martin-Martinez J.M., Characterization of EVA-based adhesives containing different amounts of rosin ester or polyterpene tackifier, *J. Adhesion*, **79**(8–9), 2003, 805–824.

79. Fujita M., Kajiyama M., Takemura A., Ono H., Mizumachi H., Hayashi S., Effects of miscibility on probe tack of natural-rubber-based pressure-sensitive adhesives, *J. Appl. Polym. Sci.*, **70**(4), 1998, 771–776.

80. Kim D.J., Kim H.J., Yoon G.H., Effects of blending and coating methods on the performance of SIS (styrene-isoprene-styrene)-based pressure-sensitive adhesives, *J. Adhes. Sci. Technol.*, **18**(15–16), 2004, 1783–1797.

81. Yang H., Sa U., Kang M., Ryu H.S., Ryu C.Y., Cho K., Near-surface morphology effect on tack behavior of poly(styrene-b-butadiene-b-styrene) triblock copolymer/rosin films, *Polymer*, **47**(11), 2006, 3889–3895.

82. Aran-Ais F., Torro-Pala A.M., Orgiles-Barcelo A.C., Martin-Martinez J.M., Addition of rosin acid during thermoplastic polyurethane synthesis to improve its immediate adhesion to PVC, *Int. J. Adhes. Adhes.*, **25**(1), 2005, 31–38.

83. Aran-Ais F., Torro-Palau A.M., Orgiles-Barcelo A.C., Martin-Martinez J.M., Characterization of thermoplastic poly-urethane adhesives with different hard/soft segment ratios containing rosin as an internal tackifier, *J. Adhes. Sci. Technol.*, **16**(11), 2002, 1431–1448.

84. Hayashi S., Kim H.J., Kajiyama M., Ono H., Mizumachi H., Zufu Z., Miscibility and pressure-sensitive adhesive perform-ances of acrylic copolymer and hydrogenated rosin systems, *J. Appl. Polym. Sci.*, **71**(4), 1999, 651–663.

85. Kim B.J., Kim S.E., Do H.S., Kim S., Kim H.J., Probe tack of tackified acrylic emulsion PSAs, *Int. J. Adhes. Adhes.*, **27**(2), 2007, 102–107.

86. Downs A.M.R., Sansom J.E., Colophony allergy: A review, *Contact Dermatitis*, **41**(6), 1999, 305–310.

87. Schuller W.H., Lawrence R.V., Culberts B.M., Some polyimide-amides from maleopimaric acid, *J. Polym. Sci. A1 Pol. Chem.*, **5**(8PA1), 1967, 2204–2207.

88. Maiti M., Maiti S., Polymers from renewable resources. 5. Synthesis and properties of a polyamideimide from rosin, *J. Macromol. Sci. Chem.*, **A20**(1), 1983, 109–121.

89. Ray S.S., Kundu A.K., Maiti M., Ghosh M., Maiti S., Polymers from renewable resources. 7. Synthesis and properties of polyamideimide from rosin–maleic anhydride adduct, *Angew. Makromol. Chem.*, **122**(JUN), 1984, 153–167.

90. Kundu A.K., Adhikari B., Ray S.S., Maiti M.M., Maiti S., Compatibility of polyblends of polyamideimide from rosin and novolac, *Abstr. Pap. Am. Chem. Soc.*, **188**(AUG), 1984, 49–50

91. Ray S.S., Kundu A.K., Ghosh M., Maiti S., A new route to synthesize polyamideimide from rosin, *Eur. Polym. J.*, **21**(2), 1985, 131–133.

92. Ray S.S., Kundu A.K., Maiti S., Polymers from renewable resources. 9. Synthesis and properties of a polyamideimide from rosin, *J. Macromol. Sci. Chem.*, **A23**(2), 1986, 271–283.

93. Kundu A.K., Ray S.S., Adhikari B., Maiti S., Polymer blends. 2. Compatibility and thermal-behavior of blends of novolac and polyamideimide from rosin, *Eur. Polym. J.*, **22**(5), 1986, 369–372.

94. Kundu A.K., Ray S.S., Maiti S., Polymer blends. 4. Blends of resol with polyamideimide synthesized from rosin, *Eur. Polym. J.*, **22**(10), 1986, 821–825.

95. Kundu A.K., Ray S.S., Mukherjea R.N., Maiti S., Polymer blends. 3. Preparation and evaluation of the blends of shellac with polyamideimide from rosin, *Angew. Makromol. Chem.*, **143**, 1986, 197–207.

96. Ray S.S., Kundu A.K., Maiti S., Polymers from renewable resources. 12. Structure property relation in polyamideimides from rosin, *J. Appl. Polym. Sci.*, **36**(6), 1988, 1283–1293.

97. Bicu I., Mustata F., Water soluble polymers from Diels–Alder adducts of abietic acid as paper additives, *Macromol. Mater. Eng.*, **280**(7–8), 2000, 47–53.

98. Mustata F., Bicu I., Polyhydroxyimides from resinic acids, *Polimery*, **45**(4), 2000, 258–263.

99. Kim S.J., Kim B.J., Jang D.W., Kim S.H., Park S.Y., Lee J.H., Lee S.D., Choi D.H., Photoactive polyamideimides synthe-sized by the polycondensation of azo-dye diamines and rosin derivative, *J. Appl. Polym. Sci.*, **79**(4), 2001, 687–695.

100. Roy S.S., Kundu A.K., Maiti S., Polymers from renewable resources. 13. Polymers from rosin acrylic-acid adduct, *Eur. Polym. J.*, **26**(4), 1990, 471–474.

101. Bingham J.F., Marvel C.S., Preparation and polymerization of a diisocyanate from Diels–Alder adduct of levopimaric acid and acrylic acid, *J. Polym. Sci. A1 Pol. Chem.*, **10**(3), 1972, 921–929.

102. Krivoguz Y.M., Yuvchenko A.P., Pesetskii S.S., Bei M.P., Functionalization of polyethylene with peroxy-containing for-mulations derived from resins modified with maleic anhydride. Properties of blends of functionalized polyethylene with polyamide 6, *Russ. J. Appl. Chem.*, **77**(6), 2004, 976–982.

103. Atta A.M., El-Saeed S.M., Farag R.K., New vinyl ester resins based on rosin for coating applications, *React. Funct. Polym.*, **66**(12), 2006, 1596–1608.

104. Atta A.M., El-Saeed S.M., Farag R.K., Synthesis of polyunsatuated polyester resins based on rosin acrylic acid adduct for coating applications, *React. Funct. Polym.*, **67**(9), 2007, 459–563.

105. Atta A.M., Nassar I.F., Bedawy H.M., Unsaturated polyester resins based on rosin maleic anhydride adduct as corrosion protections of steel, *React. Funct. Polym.*, **67**(7), 2007, 617–626.

106. Bicu I., Mustata F., Diels–Alder polymerization of some derivatives of abietic acid, *Angew. Makromol. Chem.*, **264**, 1999, 21–29.

107. Atta A.M., Mansour R., Abdou M.I., Sayed A.M., Epoxy resins from rosin acids: Synthesis and characterization, *Polym. Advan. Technol.*, **15**(9), 2004, 514–522.

108. Bicu A., Mustata F., Polymers from a levopimaric acid-acrylonitrile Diels–Alder adduct: Synthesis and characterization, *J. Polym. Sci. Polym. Chem.*, **43**(24), 2005, 6308–6322.

109. Atta A.M., Mansour R., Abdou M.I., El-Sayed A.M., Synthesis and characterization of tetra-functional epoxy resins from rosin, *J. Polym. Res.*, **12**(2), 2005, 127–138.

110. Kim W.S., Jang H.S., Hong K.H., Seo K.H., Synthesis and photocrosslinking of poly(vinylbenzyl abietate), *Macromol. Rapid Commun.*, **22**(11), 2001, 825–828.

111. Sinclair R.G., Berry D.A., Schuller W.H., Lawrence R.V., Polycondensation of resin-acid dimers with diamines, *J. Polym. Sci. A1 Pol. Chem.*, **9**(3), 1971, 801–804.

112. Kuusipalo J., PHB/V in extrusion coating of paper and paperboard: Part I: Study of functional properties, *J. Polym. Environ.*, **8**(1), 2000, 39–47.

113. Kuusipalo J., PHB/V in extrusion coating of paper and paperboard – Study of functional properties. Part II, *J. Polym. Environ.*, **8**(2), 2000, 49–57.

114. Jipa S., Zaharescu T., Setnescu R., Setnescu T., Brites M.J.S., Silva A.M.G., Marcelo-Curto M.J., Gigante B., Chemiluminescence study of thermal and photostability of polyethylene, *Polym. Int.*, **48**(5), 1999, 414–420.

115. Zaharescu T., Jipa S., Setnescu R., Wurm D., Brites M.J.S., Esteves M.A.F., Marcelo-Curto M.J., Gigante B., Effects of some secondary amines on the oxidation of ethylene–propylene elastomers, *Polym. Degrad. Stabil.*, **68**(1), 2000, 83–86.

116. Zaharescu T., Jipa S., Setnescu R., Brites J., Esteves M.A., Gigante B., Synergistic effects on thermal stability of ethylene–propylene elastomers stabilized with hindered phenols and secondary amines, *Polym. Test.*, **21**(2), 2002, 149–153.

117. Leach R.H., Pierce R.S., *The printing ink manual*, Dordrecht, Kluwer Academic Publishers, 1993.

118. Pekarovicova A., Bhide H., Fleming P.D., Pekarovic J., Phase-change inks, *J. Coating Technol.*, **75**(936), 2003, 65–72.

119. Ramani C.C., Puranik P.K., Dorle A.K., Study of diabietic acid as matrix forming material, *Int. J. Pharm.*, **137**(1), 1996, 11–19.

120. Pathak Y.V., Dorle A.K., Evaluation of pentaerythritol (rosin) estergum as coating materials, *Drug Dev. Ind. Pharm.*, **12**(11–13), 1986, 2217–2229.

121. Pathak Y.V., Dorle A.K., Evaluation of propylene–glycol rosin ester as microencapsulating material and study of dissolution kinetics, *Drug Dev. Ind. Pharm.*, **14**(15–17), 1988, 2557–2565.

122. Pathak Y.V., Nikore R.L., Dorle A.K., Study of rosin and rosin esters as coating materials, *Int. J. Pharm.*, **24**(2–3), 1985, 351–354.

123. Satturwar P.M., Fulzele S.V., Joshi S.B., Dorle A.K., Evaluation of the film-forming property of hydrogenated rosin, *Drug Dev. Ind. Pharm.*, **29**(8), 2003, 877–884.

124. Fulzele S.V., Satturwar P.M., Dorle A.K., Novel biopolymers as implant matrix for the delivery of ciprofloxacin: Biocompatibility, degradation, and *in vitro* antibiotic release, *J. Pharm. Sci.*, **96**(1), 2007, 132–144.

125. Fulzele S.V., Satturwar P.M., Dorle A.K., Study of the biodegradation and *in vivo* biocompatibility of novel biomaterials, *Eur. J. Pharma. Sci.*, **20**(1), 2003, 53–61.

126. Fulzele S.V., Satturwar P.M., Dorle A.K., Polymerized rosin: Novel film forming polymer for drug delivery, *Int. J. Pharm.*, **249**(1–2), 2002, 175–184.

127. Lee C.M., Lim S., Kim G.Y., Kim D., Kim D.W., Lee H.C., Lee K.Y., Rosin microparticles as drug carriers: Influence of various solvents on the formation of particles and sustained-release of indomethacin, *Biotechnol. Bioprocess Eng.*, **9**(6), 2004, 476–481.

128. Choudhary G., Kumar J., Walia S., Parsad R., Parmar B.S., Development of controlled release formulations of carbofuran and evaluation of their efficacy against Meloidogyne incognita, *J. Agric. Food Chem.*, **54**(13), 2006, 4727–4733.

129. Dhanorkar V.T., Gogte B.B., Dorle A.K., Formation and stability studies of multiple (w/o/w) emulsions prepared with newly synthesized rosin-based polymeric surfactants, *Drug Dev. Ind. Pharm.*, **27**(6), 2001, 591–598.

130. Dhanorkar V.T., Gawande R.S., Gogte B.B., Dorle A.K., Development and characterization of rosin-based polymer and its application as a cream base, *J. Cosmetic Sci.*, **53**(4), 2002, 199–208.

131. Snow R., Zhang J.P., Miller J.D., Froth modification for reduced fuel oil usage in phosphate flotation, *Int. J. Miner. Process.*, **74**(1–4), 2004, 91–99.

132. Gopal R., Polymer concrete composites for enhancement of mobility of troops in desert operations, *Mater. Sci. Eng. B Solid St. Mater. Adv. Technol.*, **132**(1–2), 2006, 129–133.